Geochemical Fractionation of Heavy Metals In Soils

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Abstract

The geochemical fractionation of lead, zinc, cadmium, copper and nickel in soil profiles was investigated in relation to the soil properties and composition: pH, organic matter content, amorphous iron oxides and cation exchange complexation. A modified version of the Tessier sequential extraction scheme was developed on a brown earth soil profile at Hallen (site HA) west of Bristol, which receives heavy metals from the lead/zinc metals smelter at Avonmouth. Three different soil types, a neutral stagnogley, a pH 4 podzol and a pH 4 acidic brown earth, that had received similar aerial deposition of heavy metals, principally from a disused nineteenth century metal smelter at Ringinglow, near Sheffield, were studied. The comparison of the geochemical fractionation of heavy metals in these soil types allowed the influence of soil properties on metal speciation to be examined. The theoretical mechanisms of heavy metal complexation by organic matter are reviewed and related to those observed in the humic components of organic matter extracted from the soil profiles.

At Hallen, site HA, the geochemical fractionation of lead, zinc, cadmium and copper was investigated and related to the chemical properties and composition of the brown earth soil profile. The results confirmed the pH related mobilisation of cadmium and zinc in the surface profiles, reported in other studies using different extraction techniques. In the case of Ringinglow the differences in the geochemical fractionation of each of the heavy metals in the different soil types were investigated, together with differences between the metals. The variation in the speciation of lead in the three soil types was explained by differences in soil pH. The proportion of lead in available forms was highest in the acidic soil profiles. Copper was found to be strongly associated with the organic matter phase in all three soil profiles.

Studies of humic substances, from all four soil profiles, showed that organic matter complexation of copper was by the mechanism of inner sphere complexation, whilst cadmium was associated with organic matter by cation exchange complexation. The results also indicated that zinc was complexed to organic matter by outer sphere complexation. Lead was expected to form inner sphere complexes with soil organic matter, however, these were not observed, lead appeared to be associated with organic matter by outer sphere complexation.

Although the interaction of heavy metals with soil components cannot be predicted from a knowledge of the soil properties, pH was the single most important soil property and in many situations was a major factor in determining the speciation of heavy metals almost independently of other soil factors.

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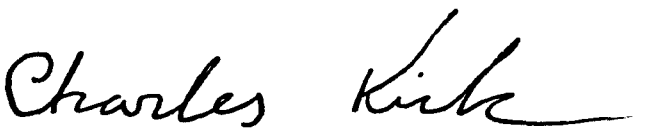
Memorandum

The work described in this dissertation was carried out in the Department of Biogeochemistry at the University of Bristol, under the supervision of Dr G. Nickless and Dr S. M. Ross. All observations and results reported are original, unless otherwise stated. No part of this work has been submitted for a degree at this or any other university.



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1.1 The Fate of Heavy Metals in Soils

The mobility of heavy metals in soils and their uptake by organisms is of considerable environmental concern, due to their potential toxicity at high concentrations. The chemical forms of heavy metals and their interactions with soil components, such as organic matter and iron and manganese oxides, determine their mobility and potential for uptake by organisms. The variety of soil components and the chemical forms that heavy metals can take renders these systems extremely complex.

Speciation is the process by which an element or molecule reacts with the components of a soil or sediment to form various species, chemical entities including: ions, molecules and solid phases. Metals in forms that may potentially be taken up by plants are termed available, the term bioavailable is usually used when the plant uptake has been measured and related to the chemical forms of heavy metals in the soil.

There are three key factors that influence the speciation of metal elements in soils:

(i) the chemical form of the element,

(ii) the mode of entry of the element into the soil profile,

(iii) the matrix characteristics of the soil profile.

The chemical form of a metal entering the soil determines the rate at which it may interact with different soil components. To facilitate the study and understanding of the speciation of heavy metals in soils, which is extremely complex, it is clear that the system chosen should be as straightforward to determine as possible. Aerial inputs of metals to soils tend to be relatively simple chemical compounds such as oxides and sulphides. Sewage sludge applications are much more difficult to investigate as the heavy metals present may enter the soil in a great variety of chemical forms, particularly as complexes by interaction with a multiplicity of different organic substances.

The direction of entry of the metal input to the soil is critical to the study of heavy metal mobility, transport and leaching down a soil profile. Sewage sludge applications are frequently mixed into the top layers of the soil causing disturbance of the upper profiles of the soil. Aerial deposition results in metals being deposited at the top of the undisturbed soil profile, instead of being mixed into several profiles, enabling the mobilisation of the metals in the soil profile to be examined. The soil properties, such as pH, iron and manganese oxides and organic matter content, then determine the speciation of the heavy metals in the profile.

Previous studies of heavy metal speciation in different soil types have shown that soil properties, particularly pH, exert a strong influence on the heavy metal speciation in soil profiles (Scokart et al., 1983). To study the effect of soil composition and chemical properties on the speciation of heavy metals, soil types were chosen that had large differences in the soil properties of interest. The associations of heavy metals with iron and manganese oxides are of considerable interest, given their large capacity as a sink for adsorbing metals. The complexation of heavy metals by the humic components of organic matter is an important control on their mobility in soils, due to the formation of either soluble or insoluble chelation complexes. The decomposition of organic matter is particularly important as it may result in the release of organic bound heavy metals.

1.2 Heavy Metal Elements

Classification

The term heavy metals is used loosely to describe metals in the environment, usually in the context of micronutrients or environmental pollution. However, a strict definition of heavy metals is those metals with a specific gravity > 5 (Lapedes, 1974).

Heavy metal elements may be divided into two groups (Morgan, 1987):

(i) micronutrients, elements essential for life including:
Na, K, Mg, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo.

(ii) potentially hazardous elements which are either micronutrients at toxic concentrations, or nonessential elements:
Cr, Cu, Zn, As, Se, Ag, Cd, In, Sn, Sb, Hg, Ti, Pb, Bi.

Choice of Heavy Metal Elements for the Present Study

The heavy metals lead, zinc, cadmium, copper and nickel were chosen for investigation in the present study. By analysing a number of different heavy metals, it is possible to investigate differences in the metal distributions that relate to the chemical properties of the elements, influencing their speciation in the soil profile. Lead and zinc have been smelted since before Roman times. As a result, there are a number of sites where they are present at high concentrations. Cadmium is of particular environmental interest due to its tendency to occur in highly soluble forms. The interaction of copper with organic matter is of particular interest, due to its strongly bound chelation complexes with humic substances. Using soils with high levels of heavy metal contamination, which are of greater environmental concern, facilitates the analytical determinations of these metals in chemical extractions.

1.3 Chemical Bonding and Classification

The geochemical fractionation of heavy metals in soils is different for each metal and is, therefore, a function of the chemical form and hence the electronic configuration of the specific metal elements. Consideration of the individual electronic configurations of each of the various heavy metals in relation to their speciation may be possible, but is probably too complex to improve our understanding of the factors controlling heavy metal speciation. Various studies have attempted to classify the metal elements in a way that is more meaningful in terms of their environmental chemistry than the term heavy metals (Pearson, 1968a; 1968b; Nieboer and Richardson, 1980; and Morgan, 1987). These classification schemes are based on the chemical properties and reactivity of the elements.

Three main types of chemical reaction are important to understanding the behaviour of pollutants in the environment:

(i) Co-ordination reactions, where electron pairs are shared between the atoms with the formation of a covalent bond,

(ii) Redox reactions, electrons are transferred between atoms or ions with the formation of an ionic bond,

(iii) Free radical reactions, important in atmospheric chemistry, such as ozone depletion, but not in heavy metal speciation in soils.

Co-ordination and redox reactions are illustrated in Figure 1.1. Of these, co-ordination reactions between metals and ligands best describe the acid-base disturbance in ecosystems caused by heavy metal pollution or acid precipitation (Morgan, 1987).

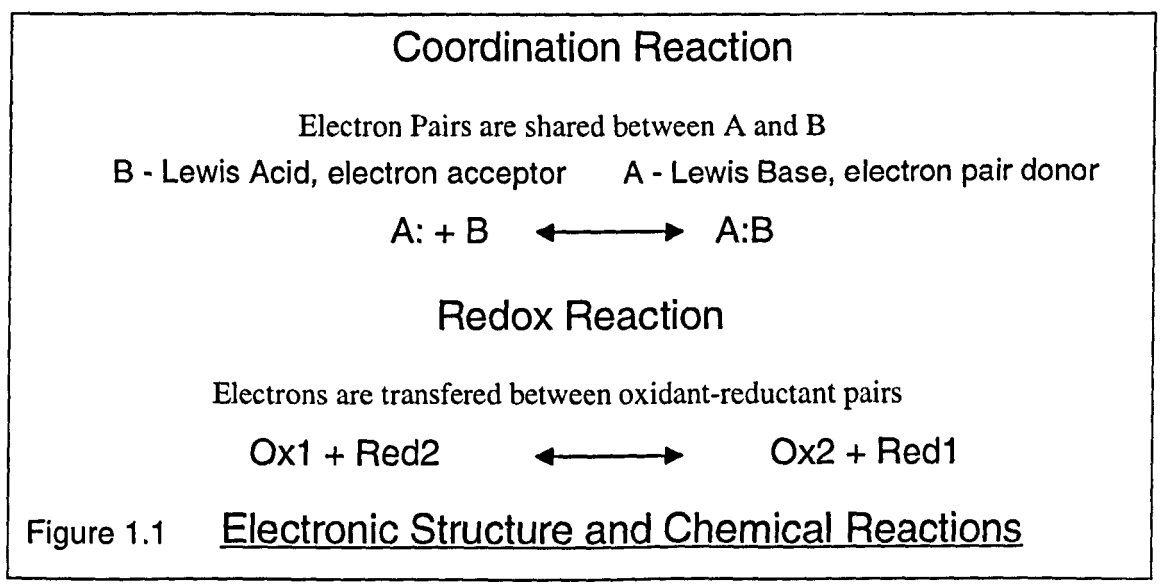


Figure 1.1 Electronic Structure and Chemical Reactions

Classification of Heavy Metals by Their Chemical Properties

Nieboer and Richardson (1980) divided metals into three distinct groups based on their differing orders of preference for ligands (Table 1.1), estimated by determining the magnitudes of the equilibrium constants. No order of preference was given for the borderline metals, as it depends on the chemical conditions prevailing in the soil. The classification was based on thermodynamic principals, independent of kinetic considerations. In soil systems, soil pH is important as metal ions compete with hydrogen ions for binding sites and bond formation requires deprotonation of the ligand.

$$M + HL \underset{\rightarrow}{\overset{\leftarrow}{}} ML + H \qquad \text{M is the metal ion, L is the ligand}$$

$$K_{ML} = \frac{[ML]}{[M].[L]} \qquad K_{ML} \text{ is the equilibrium constant}$$

Table 1.1 Classification of Metal Ions

The table relates the Pearson classification of metals into hard, intermediate and soft donors and acceptors, to the Nieboer class A, borderline and class B metal classification. Examples of the metals in each class are given, together with their preferences for ligands.

Pearson (1968a,b)	Hard acceptor Hard donor	Intermediate acceptor Intermediate donor	Soft acceptor Soft donor
Nieboer and Richardson (1980)	Class A	Borderline	Class B
Metals In Classes	K^+, Na^+, Mg^{2+}, Ca^{2+}	Pb^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Fe^{2+}, Mn^{2+}	Cu^+, Pb^{4+}
Ligands	$F^- > Cl^- > Br^- > I^-$		$I^- > Br^- > Cl^- > F^-$
Metal Binding Atoms in Ligands	O > S ~ Se O > N > S		Se ~ S > O & As > N S > N > O

Ionic and Covalent Bond Formation

Electronegativity is defined as the power of an element to attract electron pairs and form covalent bonds and is a measure of the energy of the empty valence orbital of an ion. In a co-ordination reaction, a covalent bond is formed when the metal receives electron density, which reduces its charge. In a redox reaction when there is a large difference in the electronegativity of two elements, the bonding is ionic, as electrons are transferred from the electron donor (or cation) to the electron acceptor (or anion). Where bonds are formed

between 2 elements with slightly differing electronegativities, a covalent bond is formed. Bonds with 100% covalent character are formed between atoms of equal electronegativity such as:

O — O Cl — Cl H — H

Most bonds have a mixture of ionic and covalent character as a result of an uneven distribution of charge across the molecule and polarisation of the bond. The ionic potential of a metal ion is defined as the ratio of charge to size and is used as an estimate of the tendency to form ionic bonds. A covalent index may be calculated that measures the relative importance of ionic and covalent character in a bond and is defined as:

$X^2_m r$ X_m is the metal-ion electronegativity, r is the ionic radius

The covalent index is the quotient of the valence orbital energy divided by the ionic energy (Nieboer and Richardson, 1980). Similarly, an ionic index may be defined as the square of the ionic charge divided by the ionic radius.

Z^2/r Z is the valency of the metal ion r is the ionic radius

The metals were then classified by their covalent index (Nieboer and Richardson, 1980). Class A metals were defined as those with a covalent index less than 1.75, class B metals were those that had a covalent index above 3.4 and borderline metals were defined as metals with a covalent index between 1.75 and 3.4. Macronutrient elements, such as sodium and calcium are usually class A metals, whereas micronutrient elements, for example copper and zinc, tend to be borderline metals (Sposito, 1986). The metals examined in the present study, lead, zinc, cadmium, copper, nickel, iron and manganese all fall into the borderline category. The +1 valency of copper and the +4 valency of lead are classified as class B metals in this classification, but these species are not normally found in soil systems.

1.4 Sources of Heavy Metals in the Environment

Origins

All heavy metals occurring in the biosphere originated in the earth's crust. The key environmental concern has been the anthropogenic release of heavy metals from the earth's crust, at rates far higher than those due to natural weathering. These metals are then released into the biosphere where they may become a hazard to plants and animals.

The mining of heavy metals may result in their release into the environment, both from the wind dispersal of the metal ore as dust and from mine tailings. Metals are released by smelting and processing into the atmosphere as particulate emissions and aerosols. In one sense the origin of metals emitted by the burning of fossil fuels is different to that of metals released through the processes of mining metal ores. Metals so released were originally in the biosphere in the organisms that became coal or oil. It could therefore be argued that the ultimate origin of these metals was natural weathering.

Overall, there are two main pathways by which heavy metals may enter the biosphere:

(i) Natural weathering of mineral rock,

(ii) Anthropogenic sources.

The present study investigates the geochemical fractionation of heavy metals from aerial deposition. The various anthropogenic sources of heavy metals are described in Table 1.2. The result of the processing of these metals tends to increase their availability to plants.

Table 1.2 Anthropogenic Sources of Heavy Metals in the Environment

After Ross 1994a.

Process	*Sources of Heavy Metals*	*Heavy Metals*
Mining of Metal Ores	Mine Tailings	Depends on the ore extracted lead, zinc, cadmium, copper etc.
Atmospheric Deposition	High temperature combustion Non-ferrous metal industries Fossil Fuel combustion Vehicle exhaust emissions	lead, zinc, cadmium, copper, etc.
Industrial Processes	Oil Refinery Petroleum industry Iron and Steel production	nickel, chromium and lead
Agriculture	Fertilisers Pesticides	Cadmium in phosphate fertilisers Copper in fungicides
Waste Disposal	Sewage Sludge applications	cadmium, chromium, copper, nickel, lead, zinc,...etc

Natural versus Anthropogenic Sources of Heavy Metals in the Environment

To attempt to estimate the potential for contamination from various heavy metals, indices of relative pollution potential have been devised. The technophility index proposed by

Nikiforova and Smirnova (1975) is defined as the ratio of annual mining activity to the mean concentration of the heavy metal in the Earth's crust. The highest ratios have been calculated for cadmium, lead and mercury, indicating the importance of these metals to man and the potential for contamination of the environment.

Another approach used to estimate the enrichment of heavy metals in the environment, due to man's activities, has been to calculate the natural and anthropogenic fluxes of these metals into the atmosphere or the oceans. A "mobilisation factor" may then be calculated as the ratio of anthropogenic emissions to natural emission. Estimates of the atmospheric natural and anthropogenic emissions together with mobilisation factors are shown in Table 1.3 for the metals lead, zinc, cadmium and copper (Lantzy et al., 1979). The much higher estimates of anthropogenic emission of these heavy metals, particularly lead, compared to their natural emission levels illustrates their importance as a source of metal contamination in soils.

Table 1.3 Mobilisation Factors for Atmospheric Sources of Heavy Metals

Source: Lantzy et al. (1979)

Element	*Natural Emissions*	*Anthropogenic Emissions*	*Mobilisation Factor*
Cadmium	0.29	5.5	19
Copper	19	260	13
Lead	4	400	100
Zinc	36	840	23

The two main ways that the relative importance of natural and anthropogenic emissions of heavy metals may be determined are by:

(i) analysis of the historical trends in metal deposition,

(ii) comparing the metal concentrations in wet deposition at locations in close proximity to potential sources with areas remote from possible sources of heavy metal contamination (Campbell et al., 1983).

Historical trends are difficult to determine due to the lack of systematically collected experimental data. Many studies have investigated wet deposition in ecosystems in relation to distance from the likely source of metal contamination, e.g. Grigal and Ohmann (1989).

In the UK, atmospheric deposition of heavy metals has been shown to be the largest source of metals to agricultural land (Critchley, 1983). The study found that over 75% of copper, nickel, lead, zinc, arsenic and selenium was from aerial deposition. However, for the

metals cadmium, chromium and mercury, atmospheric deposition was shown to account for less than half of the metal entering the soils. Long term studies of cadmium concentrations in archived soils from 1860 onwards at Rothamsted Experimental Station, one of the few studies of historical trends in metal deposition, have shown that phosphate fertilisers are a significant source of cadmium in agricultural soils (Jones et al., 1987; 1992). Gulson et al. (1981) identified the source of lead contamination in Australian soils by analysis of the lead isotopes which differed depending on the mineral source of the metal.

Aerial Deposition of Heavy Metals

There are three main types of aerial deposition:

(i) Crustal weathering, a low temperature process,

(ii) Volcanic activity, a high temperature process,

(iii) Anthropogenic activities, combustion process e.g. smelting.

The present study investigates the speciation of anthropogenic aerial deposition of heavy metals in soils. However, comparisons with natural emissions provide useful insights into the mechanisms by which aerial deposition interacts with soils. Deposition of heavy metals from the atmosphere takes place in the form of dry, wet and occult precipitation. Dry deposition is in the form of gaseous compounds and aerosols. Wet deposition occurs where heavy metals are washed out of the atmosphere by precipitation. Occult deposition is the deposition of heavy metals in fog and clouds, usually at high altitudes.

The particles derived from crustal weathering are produced at low temperatures. In contrast, anthropogenic deposition is usually produced by high temperature combustion processes such as metal smelting, fossil fuel combustion and waste incineration. As a result, there are important differences in the chemical reactivities of particles from these different sources. Combustion processes tend to result in the condensation of heavy metals, or their compounds, on the surface of fly ash particles at high temperatures. The presence of heavy metal compounds on the surface of the particles increases their reactivity compared to crustal derived particles, where metals are embedded in the particle matrix (Chester et al., 1986).

The main factor influencing the level of surface accumulation of heavy metal deposition from aerial sources is the distance from the source (Esser et al., 1991). A non-linear regression model of cadmium and lead concentrations in soils in relation to their distance from the smelter source has been described by Godin et al. (1985). The interaction of aerial deposition with vegetation has been reviewed by Bergkvist et al. (1989). Topology was shown

to be an important factor in determining the extent of aerial deposition of heavy metal elements. Deposition was found to be greater at the edges of forests and on hill tops resulting in considerable spatial variation in wet deposition. Foliar interception of dry deposition was observed to be much greater for a forest canopy than for pasture. Coniferous forests have been shown to be more efficient at trapping dry deposition than deciduous forests (Mayer and Ulrich, 1982). Occult deposition by fog and cloud has also been shown to be important at high altitudes (Lovett et al., 1982). Although the volume of throughfall water from a canopy has been shown to be reduced by around 25%, the heavy metal contents were found to be significantly higher than the amount deposited by wet deposition on the canopy (Bergkvist et al., 1989). The metal concentrations were much higher under coniferous trees than under deciduous trees which have larger leaves but a smaller total leaf area.

Chemical Forms of Aerial Deposited Heavy Metals

The chemical reactivity of heavy metals that have been deposited on soil profiles by aerial deposition depends on their particular chemical structure and the chemical properties of the soil such as soil pH. Where metals incident on the soil are in the form of insoluble salts (for example lead sulphate) they are unlikely to react rapidly with the soil components compared to more soluble salts. Heavy metals have been classified according to the volatility of the elements and their chemical species.

The reactivity of the heavy metals in aerial deposition depends on whether the metal is present on the surface of the fly ash particles, or in the matrix of the particle (Davidson et al.,1974). The metal distribution depends on the volatility of the element and the presence of other elements, including, chlorine, oxygen and sulphur. Metals have been placed in four classes (Table 1.4) depending on their boiling points and volatilisation potentials (Klein et al., 1975).

Table 1.4 Klein Classification of Metal Elements Depending on their Boiling Points

After Klein et al. (1975)

Class	*Metal*	*Behaviour*
Class I	Al, Ba, Ca, Co, Fe, K, Mg, Mn, Si, Sr, and Ti	Metals with high boiling points that are not volatilised in the combustion area and make up the matrix of fly ash.
Class II	As, **Cd**, **Cu**, Ga, **Pb**, Sb, **Zn** and Se	These metals are volatilised during combustion. On cooling they condense on the surface of fly ash particles.
Class III	Hg	Metal remains in the gas phase throughout the process.
Class IV		Metals whose behaviour is a mixture of two or more of the above classes.

The presence of chlorides, oxides and sulphide ligands depends on the type of combustion process taking place. During the incineration of municipal waste, the presence of polyvinyl chloride plastics provides a source of hydrogen chloride (Fernández et al., 1992), which is not present in either fossil fuel combustion or in metal smelting. Both fossil fuel combustion of sulphur containing coals (Eary et al., 1990) and the smelting of metal sulphide ores result in the production of sulphuric acid. The presence of sulphur and oxygen in these processes suggests that metal oxides and sulphates are important components of aerial deposition from these sources. The likely chemical species present in aerial deposition from anthropogenically derived processes (Table 1.5) have been determined by Pacyna (1987).

Table 1.5 Chemical Species in Aerial Deposition Derived from Anthropogenic Processes

Based on: Eary et al. (1990), Fernández et al. (1992) and Pacyna (1987).

Process	*Cadmium*	*Lead*
Coal Combustion	CdO, CdS	Pb, PbO, PbS
Oil Combustion		PbO
Metal Smelting	CdS, CdO	PbO, $PbSO_4$
Municipal Waste Incineration	$CdCl_2$, CdO	Pb, $PbCl_2$, PbO

1.5 Soil Processes and Heavy Metal Speciation

The reactions of heavy metals with the soil components determines their potential availability and mobility in the soil profile. The transformation of metals between soluble and insoluble chemical species is controlled by a variety of soil processes and soil chemical properties. The main processes controlling the geochemical fractionation of heavy metals in soils are:

(i) Exchange onto cation exchange sites of soil components,

(ii) Adsorption onto the oxides and hydroxides of iron, manganese and aluminium,

(iii) Complexation with organic ligands.

The interactions of heavy metals and organic matter are described in detail in Chapter 3. Detailed reviews of soil properties in relation to metal fractionation are given in Ross (1994b) and McBride (1989).

Heavy Metal Binding to Exchange Sites

Heavy metals may be exchange complexed to organic matter or clays by non-specific electrostatic attraction. The importance of cation exchange complexation is that it reduces the mobility of heavy metal ions in the soil, but leaves the solubility of the ions unaffected (McBride, 1989). Heavy metals compete for cation exchange sites on layer silicates and organic matter with the class A metals, in particular calcium and magnesium. As heavy metals are usually present at low concentrations relative to these metals, strong exchange complexation is unusual. Berggren (1992) showed that exchange complexation of cadmium was the main control on cadmium solubility in podzols. Cation exchange complexation was also observed to be the process controlling cadmium mobility in uncultivated natural soils in a study by Sánchez-Martin and Sánchez-Camazano (1993). The exchange complexation of zinc and copper has been found to be inhibited by the presence of calcium, magnesium and potassium (Zhu and Alva, 1993a). The sorption of both zinc and copper decreased with increasing calcium concentrations.

Adsorption to Amorphous Iron, Manganese and Aluminium Oxides

Adsorption takes place when heavy metals are bound to surfaces by non-exchange complexation. Unlike cation exchange complexation the process involves the formation of chemical bonds between the heavy metal cation and the surface. Adsorption of heavy metals to amorphous iron and manganese oxides plays a major role in limiting their solubility and hence their availability and mobility in soils and sediments. These oxide substrates are particularly important owing to their high adsorption capacity for heavy metals. The main soil property controlling the retention of these metals on iron and manganese oxides is pH. In general as the soil pH increases from acidic toward neutrality, the affinity of heavy metals for these oxides increases.

A number of studies have investigated the retention of heavy metals on freshly prepared gel iron oxides and gel manganese oxides (Kinniburgh et al., 1976 and McKenzie, 1980). These studies have shown that there are important differences in the affinities of heavy metals for such substrates. Heavy metals were found to be retained on iron oxides under more acidic pH conditions than the class A alkaline metals. Kinniburgh et al. (1976) observed the retention of eight metals on iron oxides and aluminium oxides including, cadmium, copper, lead and zinc under various pH conditions. Lead was displaced from the gel iron oxide when the pH was lowered below pH 3.5 and copper was displaced below pH 4.5. The displacement

of zinc took place at just below pH 6 and cadmium displacement occurred at pH 6.5. These pH values are approximate as the absorbed metal was released over a range of 1 pH unit. These results suggested that the acidification of soils would lead to the mobilisation of cadmium and zinc at a much higher pH than for lead and copper. Attempts to predict affinity sequences by using ionic potentials have not been successful, but the sequences, with the exception of cadmium, may be explained by the classification into class A, borderline and class B metals described in Section 1.3. These results give an indication of the affinity sequence that might be expected in soils. However, as soils are multi-component systems the presence of other substrates, such as manganese oxides and organic matter, may obscure the effects of amorphous iron oxides.

The retention of heavy metals on amorphous aluminium oxides has been observed to follow a slightly different order to that on iron oxides (Kinniburgh et al., 1976). The order of copper and lead was reversed and both metals were released at a higher pH from aluminium oxide. The interactions of heavy metals with soil components depend on the affinities of the metals for those soil components and the abundance of the components in the soil.

The adsorption of copper and cadmium by manganese oxides has been studied by Fu et al. (1991), by means of potentiometric titrations. Both copper and cadmium adsorption was found to increase with increasingly alkaline pH. Copper was observed to have a higher affinity for manganese oxides than cadmium at pH 5.5. Manganese oxides were found to have a high capacity for these metals.

The competitive adsorption of heavy metals by soils has been investigated by a number of workers (Table 1.6).

Table 1.6 Heavy Metal Affinity Series for Soils

Soil	*Affinity Sequence*	*Source*
24 Cultivated loam soils	Pb > Cu > Ni > Cd = Zn	Basta and Tabatabai (1993a,b)
21 Mineral and Organic soils	Pb > Cu > Zn > Ni > Cd	King (1988)
Mine contaminated Soil	Pb > Cu > Zn > Ni > Cd	Merrington & Alloway (1994)
Mineral soil pH 5	Pb > Cu > Zn > Cd	Elliott et al. (1986a)
Organic soil	Pb > Cu > Cd > Zn	

These results are similar to those obtained by Kinniburgh et al. (1976) in their laboratory experiments on synthesised gel iron oxides. The similarity of these affinity sequences for whole soils, to those obtained in studies of laboratory produced iron oxides,

suggests that iron oxides play a key role in the retention of heavy metals in soils. The difference in the two affinity sequences obtained by Elliott et al. (1986a) reflect the complexation of cadmium in the organic soil increasing its retention relative to zinc. The soil components have differing capacities and affinities for heavy metals. The substrate sorption order for lead, zinc and cadmium was determined by Kabata-Pendias (1980) as being:

Mn-oxides > Montmorillonite > Kaolinite > Fe-oxides > Illite.

Precipitation Reactions

There is considerable difficulty in distinguishing experimentally between adsorption and precipitation of heavy metals at the mineral surface, as the formation of a new solid phase may not be recognised (McBride, 1989). Adsorption/desorption processes are favoured by low heavy metal concentrations, a large number of adsorption sites and an acidic pH. Precipitation is most likely at high heavy metal concentrations and under neutral or alkaline conditions. In the case of zinc, the adsorption/desorption process has been observed to occur exclusively below pH 7, with precipitation only occurring at above pH 7 and then only at concentrations of zinc that were high enough to saturate the adsorption sites (Brummer et al., 1983).

Processes Controlling the Mobility of Heavy Metals in Soils

Cation exchange complexation, adsorption/desorption and precipitation reactions control the distribution of heavy metals between the solid and solution phases. The mobility of heavy metals in soils is then dependent on their affinity for the various soil components. Acidification of soils causes the dissolution of precipitated heavy metal phases, where these are present. The reduction in pH also leads to the release of heavy metals from adsorption sites.

1.6 Research Aims and Objectives

The present study investigates the distribution and geochemical fractionation of lead, zinc, copper, cadmium and nickel at six depths in four, widely different, soil types. Soil profiles of very different chemical properties and composition were studied to elucidate the effects of these properties on heavy metal speciation. To evaluate the overall role of pH in heavy metal speciation in soils, soil profiles of widely differing pH were chosen. The study of heavy metals that enter the soil by aerial deposition allows their speciation in the soil profile to be investigated, as they interact with the soil components and are mobilised or immobilised in

the soil profile. The aerial deposition from metal smelters provided a high degree of metal contamination, enabling the study of the small proportions of the total metal content associated with some geochemical phases.

The geochemical fractionation of heavy metals in the soils was carried out using a modified version of the Tessier sequential extraction scheme, described in Chapter 2. The selectivity of the reagents used in sequential extraction schemes and the accuracy of the heavy metal partitioning results obtained by these schemes are discussed in Section 2.1. The distribution of heavy metals, between the geochemical phases of the soil, was investigated at different depths in each soil profile to study the effect of changing soil properties with depth. The geochemical fractionation results allowed the question of whether specific soil phases are associated with specific heavy metal elements to be addressed, by comparing the heavy metal fractionation with the following estimates of soil properties and components:

(i) Cation exchange capacity,

(ii) Amorphous and crystalline iron oxides,

(iii) Total organic matter content.

The interaction of heavy metals with organic matter was investigated in different soil types. The complexation of heavy metals with organic matter is reviewed in Chapter 3. Specifically, the study investigates the role of the humic and fulvic acid components of organic matter in the mobilisation and immobilisation of heavy metals. A scheme for the extraction and fractionation of soil organic matter was developed to determine the concentrations of heavy metals in humic and fulvic acids. The strength of association between heavy metals and the organic matter components was estimated, by comparing the results of the various chemical extractions of different strengths. An attempt was made to relate the detailed analysis of heavy metal binding by humic substances, to the geochemical fractionation of heavy metals, determined in each soil profile. The combination of these techniques allowed the importance of organic matter in the complexation of heavy metals to be assessed in the overall context of metal speciation in soil profiles.

2 Partitioning of Heavy Metals In Soils

2.1 Development of Sequential Extraction Techniques

The speciation of metals in soils and sediments may be determined by three approaches:

(i) Thermodynamic modelling,

(ii) Direct determination of specific soil or sediment phases,

(iii) Extraction by chemical reagents.

Thermodynamic modelling attempts to predict metal speciation by the application of chemical kinetics, to the thermodynamic data of different chemical species. A number of problems are associated with this approach and these were discussed by Campbell and Tessier (1987). Problems exist in the characterisation of organic ligands and definition of the redox state. There is a lack of thermodynamic data for chemical species occurring in the environment under natural conditions. Our knowledge of biological and chemical processes that take place in soils and sediments is incomplete, resulting in equations that are inaccurate and inconsistent. In particular there are serious problems in the characterisation of organic ligands (Ross, 1994b; Campbell and Tessier, 1987). A more fundamental problem with the theoretical approach is that most models assume the system to be in equilibrium and fail to take account of the dynamic nature of systems in the natural environment.

The direct determination of the solid phases for a complete soil or sediment is very difficult, maybe impossible (Campbell and Tessier, 1987). Solid phases exist in a large number of different forms that are frequently amorphous. The associations of heavy metals with organic matter and iron and manganese oxides are particularly difficult to determine, as these phases frequently occur as multi-layer coatings on particles (Etcheber, 1983). In these cases the structure and nature of the coatings are important in determining the binding sites that may be available to heavy metals. Adding to the difficulty of direct determination are the very low concentrations of metal involved in normal environmental situations in soils and sediments. As a result of these difficulties a number of methods have been developed to investigate the speciation of metals in soils by chemical fractionation (e.g. Tessier et al., 1979; Griffin et al., 1989; Miller et al., 1986). A few studies have compared the results of chemical extractions with direct determinations of specific fractions. Tipping et al. (1985) compared the results from a sequential extraction procedure, with direct determination of a single specific fraction. The study investigated the distribution of heavy metals in the iron and manganese

oxides fraction. The results obtained by electron microscopy and electron probe microanalysis were then compared with those from a sequential extraction scheme. Other studies have compared the results from X-ray diffraction and sequential extraction schemes for specific fractions (e.g. Tessier et al., 1979).

2.1.1 Chemical Extraction Techniques

Total digests have been used to measure the contamination of soil by heavy metals in a vast number of studies, in a range of different ecosystems. Studies of heavy metals in the environment are interested not only in the concentrations of heavy metals in the soil, plant or sediment, but also in the chemical form of the metal and its potential for uptake by biological organisms. The mobility of the metals in soils is important particularly in relation to leaching of toxic metals into ground water supplies. Total digestions give an estimate of the maximum amount of metal that is potentially available or mobile, but the results so obtained may bear little relationship to the actual levels of available or mobile metal present in the soil.

The use of chemical extractants of increasing strength permits the extraction of metals according to their strength of bonding to the various phases in the soil. If a metal is easily removed from a phase by a weak chemical extractant, it is likely to be available for uptake by plants, or leached through the soil. This is the case for cadmium electrostatically bound to clay minerals or organic matter. Metals that are only removed from a phase by powerful extractants, such as strong mineral acids, are unavailable to organisms under normal environmental conditions and time spans. The time scale becomes important in the case of organic matter, which decomposes over time releasing the metals bound to it. This is discussed in detail in Chapter 3 which discusses organic matter.

2.1.2 Principles of Sequential Extraction

The concept behind sequential extraction is that the solid material of soils or sediments can be partitioned into specific fractions. The five fraction scheme developed by Tessier et al. (1979) was designed for the extraction of oxic sediments. In essence, the scheme took five different reagents borrowed from soil chemical analysis and put them together in a scheme. A soil or sediment sample was leached with a sequence of progressively more powerful reagents, Figure 2.1 illustrates the modified Tessier scheme used in this study. Other workers had used sequential extraction techniques, for example McLaren and Crawford (1972), but the Tessier scheme is the only scheme of its kind to be used in a large number of different studies. The use of increasingly powerful reagents allows the determination of the relative bonding strengths of

Tessier Sequential Extraction Scheme

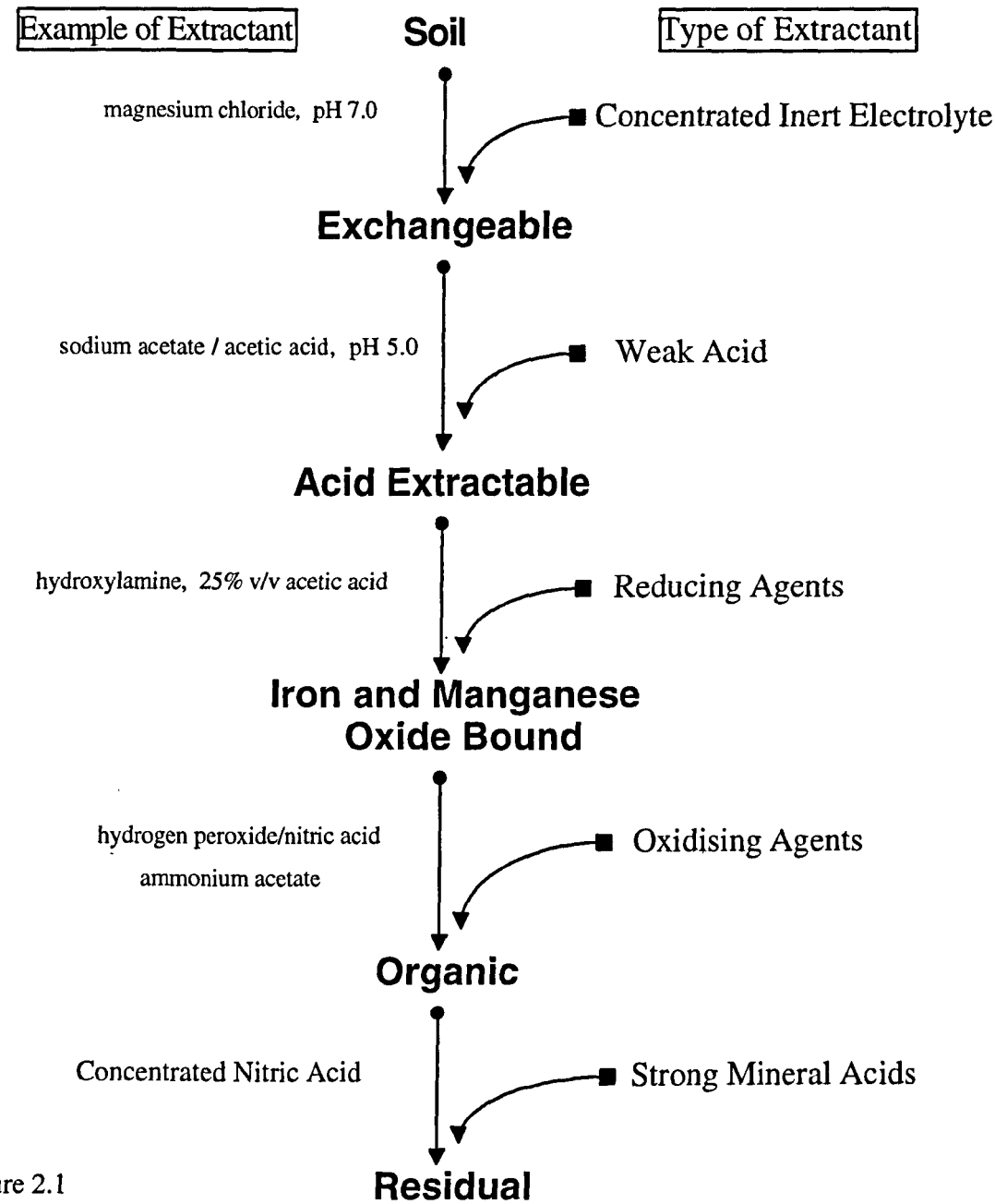


Figure 2.1

metals to different phases. The scheme offered a significant improvement over total digests for environmental work. In theory, knowledge of sequential extraction data on the partitioning of toxic metals in soils together with information on the biological uptake of metals by organisms could allow an estimate of toxicity to be made (Calmano and Förstner, 1983). Unfortunately realising this objective is very difficult and results so far have not been altogether satisfactory.

The Tessier sequential extraction scheme divides the soil into five geochemical fractions. However, other workers have used a larger number of fractions, Miller et al. (1986) defined nine fractions by subdivision of the iron and manganese oxides phase, but five fraction schemes are the most commonly used so these will be described here. The classes of reagents of similar chemical behaviour are explained below, individual reagents and their selectivity for different fractions will be described in the next section. An outline of the scheme is illustrated in Figure 2.1 and full details of the method are presented in Chapter 4. Tessier et al. (1979) and Campbell and Tessier (1987) define the different fractions as follows:

Fraction 1. (Exchangeable)

Concentrated inert electrolytes are used to displace adsorbed metals, which are labelled exchangeable, the extraction also removes soluble metals. The fraction consists of metals that are electrostatically adsorbed onto the surface of humic acids, iron and manganese hydrated oxides and some minerals. Metal in this fraction are removed using weak reagents, and are considered to be available.

Fraction 2. (Acid Extractable)

Weak acids are used to dissolve the acid extractable phases, such as carbonates and to desorb specifically adsorbed metals. The fraction so extracted is frequently called the Carbonate bound phase. However, as this implies that the metals are associated with carbonates, the term acid extractable will be used in this review. Specifically bound metals are bound either by covalent type bonds or by inner sphere chelation complexes. Metals in this fraction are likely to be available to plants, since organic acids produced in the rhizosphere will lead to dissolution of the acid extractable phases.

Fraction 3. (Bound to Iron and Manganese Oxides)

Reducing agents are used to remove metals bound to iron and manganese oxides by reduction of the oxide or oxyhydroxide phase. The fraction is defined as the iron and manganese oxides bound fraction. The iron and manganese oxides and oxyhydroxides may exist as: coatings on particles, as nodules, or as concretions, depending on the type of substrate. The fraction is an important sink for heavy metals as iron and manganese oxides are known to be scavengers of heavy metals (Tessier et al., 1979).

Fraction 4. (Organic bound)

Oxidising agents are commonly used to remove metals complexed to organic matter or associated with sulphides. The fraction is defined as the organic fraction. The destruction of

organic matter, by oxidation, leads to the dissolution of heavy metals bound to it. Metals can be complexed with humic and fulvic acids and other organic macromolecules. The oxidation of sulphides is particularly important in anaerobic sediments, where they may constitute a major fraction. Where sulphides are an important component of the substrate, an additional extraction is required, with sufficient power, to differentiate between the organic bound and sulphide associated fractions (Campbell and Tessier, 1987). Complexing agents may be used which compete with organic matter functional groups to complex metals. Complexing agents may also dissolve precipitates by complexing them into solution.

Fraction 5. (Residual)

Finally strong mineral acids are used to dissolve resistant oxides, sulphides and aluminosilicates, which are the residue of previous extractions. The residual phase is therefore composed of primary and secondary minerals and heavy metals associated with the fraction are usually bound inside the crystal lattice and are not likely to become available under normal conditions.

2.1.3 Operational Definition of the Chemical Fractions

It is immediately apparent that the chemical extractants used in sequential extraction schemes (Table 2.1) are not entirely selective in the metal forms that they remove. The labels used for different fractions, such as those associated with the acid extractable phase, or bound to organic matter are convenient because they simplify the presentation of results. However, these labels can be misleading as they imply that the reagents used are highly selective for the fractions extracted. It is important to consider the meaning of the different fractions. Campbell and Tessier (1987), Lion et al. (1982) and Tessier et al. (1979), have suggested that metal forms are classified into operationally defined fractions according to their chemical reactivity. Tessier et al. (1979) and Rapin et al. (1986), defined the distribution of metals between fractions as being operationally defined by the method of extraction. For example, in the case of the Tessier scheme, the organic phase consists of metals that are extracted with an oxidising agent, hydrogen peroxide. A similar situation exists in soil chemical analysis where, for example, iron concentrations in soils are quoted as pyrophosphate extractable iron. However, in soil chemical analysis the techniques have been standardised, measurements of iron are quoted as pyrophosphate extractable iron, making comparison between different studies and at different field sites possible. Standard reference soils are used so that different laboratories can standardise their results. The difficulty with sequential extraction techniques is that different

workers use a variety of different extractants making comparison between studies very difficult or impossible.

Table 2.1: Reagents Used in Sequential Extraction Schemes

Geochemical Phase	*Chemical Extractant*	*Conditions*	*Reference*
Exchangeable	magnesium chloride	pH 7.0	Tessier et al. (1979)
	calcium chloride	pH 7.0	McLaren & Crawford (1972)
	ammonium acetate	pH 7.0	Hickey and Kittrick (1984)
	calcium nitrate		Miller et al. (1986)
Acid Extractable	sodium acetate/acetic acid	pH 5.0	Tessier et al. (1979)
	carbon dioxide treatment of suspension		Calmano and Förstner (1983)
	acidic cation exchanger		Campbell and Tessier (1987)
Reducible	acidified hydroxylamine	+ 0.01M nitric acid	Chao (1972)
	hydroxylamine	25% acetic acid	Tessier et al. (1979)
	ammonium oxalate {amorphous iron}		Miller et al. (1986)
	dithionite-citrate buffer {crystalline iron}		Miller et al. (1986)
Organic	hydrogen peroxide	nitric acid	Tessier et al. (1979)
(+ Sulphides)	sodium pyrophosphate		Miller et al. (1986)
	sodium hypochlorite		Shuman (1983)
	DTPA / sodium acetate	pH 7.0	
Residual	hydrofluoric + perchloric acids	reflux	Tessier et al. (1979)
	hydrofluoric + nitric acids	reflux	Xian (1989)
	nitric acid	reflux	Clevenger (1990)

2.1.4 Selectivity of Chemical Extractants

To interpret sequential extractions it is necessary to consider the selectivity of the reagents that are used. A truly selective reagent would attack only a single fraction and would have no effect on the others. In practice most of the reagents employed in sequential extraction schemes have some action on the other fractions. The advantage of using a sequential extraction scheme, over using a single extractant, is that once a phase has been

extracted it can no longer interfere with the results obtained for subsequent phases. An example is that once the exchangeable fraction has been extracted it is clear that any metals found in subsequent fractions were not in the exchangeable phase. Other problems arise, such as readsorption of released metal by other phases and these will be discussed in Section 2.1.6. Inevitably, the accuracy of the procedure decreases for the fractions extracted later in the sequence. The selectivity of the various extractants used in sequential extraction schemes will now be considered.

There are a number of different ways of evaluating the selectivity of sequential extractions, these have been evaluated by Campbell and Tessier (1987). Successive extractions using a single reagent may be carried out on a single phase. Pure solids may be used: alone, as part of a model sediment, or spiked into a natural sediment. The residue left after an extraction may be analysed for other components such as: organic and inorganic carbon, total sulphur, acid volatile sulphide, aluminium and silicon. The main chemical extractants used in sequential extraction schemes were reviewed by Beckett (1989) and are listed in Table 2.1.

Exchangeable Phase

Rapin and Förstner (1983) analysed the solid residues after each extraction, for organic carbon, iron and total sulphur remaining. The experiment was carried out on both marine and freshwater sediments and the mineral phases of deep sea nodules. The result was an estimate of the selectivity of the different reagents. Using ammonium acetate at pH 7.0, as the exchangeable fraction extractant, they found that 3-10% of cadmium, lead and manganese associated with the acid extractable fraction were released. Tessier et al. (1979) obtained similar results, concluding that ammonium acetate is unsuitable for this extraction, as sodium acetate was found to reduce the efficiency of the subsequent extraction step. Magnesium chloride was suggested as the most suitable extractant for exchangeable metals.

Acid Extractable Phase

Sodium acetate at pH 5.0 is the most suitable and commonly used extractant for the removal of metals weakly bound to specific sites or carbonate phases in soils and sediments (Pickering, 1983). Tessier et al. (1979) evaluated the optimum time for the extraction to be five hours. Rapin and Förstner (1983), found that sodium acetate at pH 5.0 completely dissolved the carbonate phase. It has been suggested that this extractant may attack occluded iron and manganese oxides (Hickey and Kittrick, 1984; McLaren and Crawford, 1972). Certainly the pH of the reagent is critical, a lower pH will result in a partial attack on the iron

and manganese oxides phase. One advantage of using this reagent is that it reduces the buffering capacity of the sample before the acidic reduction of iron and manganese oxides is carried out (Calmano and Förstner, 1983).

Iron and Manganese Oxides Phase

The iron and manganese oxides fraction is a mixture of three or four types of oxide: manganese oxide, amorphous hydrous iron oxide and crystalline iron oxide. Extraction of amorphous iron oxides in soil chemical analysis is carried out by leaching with potassium pyrophosphate. Amorphous hydrous iron oxides have been divided into two types, gel and aged, although the precise difference between the two in the natural environment is unclear. Pyrophosphate extracts amorphous gel oxide at pH 10 and amorphous aged and gel hydrous oxides at pH 7, crystalline oxides are extracted using a dithionite citrate buffer at pH 3.8 (Bascomb, 1968).

Iron and manganese oxides are separated by the use of hydroxylamine hydrochloride in dilute nitric acid. Chao (1972) experimented with a range of pH, from pH 1 to pH 3, and extraction times, of 15 to 60 minutes, to selectively extract manganese oxides. Chao found that the optimal pH for the reaction was achieved using 0.1M hydroxylamine hydrochloride in 0.01M nitric acid for 30 minutes. Longer extraction times or more acidic conditions were found to increase the iron oxide extracted, while the amount of manganese extracted remained constant. Using this extraction Chao found that 85% of the total manganese and 5% of the total iron was dissolved. In soils the total iron concentration is often at least an order of magnitude higher than the total manganese concentration. This implies that in soils the heavy metals released by this extraction could be associated with the iron oxide phase. To determine whether heavy metals were associated with iron or manganese oxides it would be necessary to look at the metal concentrations with reference to the relative sizes of the different oxide phases.

The Tessier sequential extraction scheme uses hydroxylamine chloride in 25% v/v acetic acid to extract amorphous iron and manganese oxides (Campbell and Tessier, 1987). The reagent leaves the crystalline oxides intact, which are then extracted in the residual fraction. Rapin and Förstner (1983) found that the reagent was highly selective extracting 90% of the iron and 100% of the manganese from an amorphous iron manganese oxide nodule. The extractant probably also removes some aluminium hydroxides (Hickey and Kittrick, 1984). Other sequential extraction schemes extract crystalline iron oxides as a separate fraction, for

example Griffin et al. (1989) used a dithionite citrate extractant to extract heavy metals associated with amorphous and crystalline iron oxides. However, Tessier et al. (1979) had found that the dithionite reagent was contaminated with zinc, difficult to purify and caused clogging of the atomic absorption burner. Miller et al. (1986) used ammonium oxalate at 85°C with ultraviolet light to extract crystalline iron oxides.

Organic Phase

There are two main methods for the examination of the organic fraction: digestion of organic matter and dissolution of organic matter. Digestion of organic matter is carried out by oxidation, using hydrogen peroxide in nitric acid, which also removes sulphides. Potassium pyrophosphate has been used to dissolve organic matter (Miller et al., 1986). This extractant has also been used to measure amorphous iron so it is important that this step is carried out after the extraction of amorphous iron and manganese oxides. Neither of these reactions completely removes organic matter, because of the highly recalcitrant nature of some humic components. A reagent sufficiently powerful to remove all the organic matter, including the recalcitrant components, would inevitably attack other fractions.

Residual Phase

The digestion of the residual fraction has been carried out with a range of hydrofluoric acid mixtures (e.g. Tessier et al., 1979; Elliot and Shields, 1988). It is important that if the sequential extraction results are being compared to a total metal digest that the digestions are carried out by the same method. Elliot and Shields (1988) found large differences between digestion with an aqua regia hydrofluoric acid mixture and a mixture of hydrofluoric, hypochloric and nitric acids, in the analysis of lead in a highly contaminated soil. The result was probably because of an insufficient reaction time rather than a genuine difference between the methods. Nitric acid digestion has been used for the residual fraction digestion (e.g. Clevenger, 1990). It is insufficiently powerful to dissolve silicates, but given that metals bound in a crystal lattice are not available this is not considered to be a problem in studies concerned with available and potentially available metals. Nitric acid is also a safer reagent to use, an important consideration when a large number of digests are carried out.

2.1.5 The Sequence of Chemical Extractions

The order in which the extractions are carried out is of considerable importance. The aim of the extraction procedure is to avoid the dissolution of multiple phases by a single extractant. Megluellati et al. (1983) and Etcheber et al. (1983), reported that altering the order

of the Tessier scheme improved the efficiency of the extraction procedure in studies of estuarine sediments. The improvement was attributed to the removal of organic matter coatings which can block the extraction of other phases, such as iron and manganese oxides. The oxidation of organic matter was carried out after the exchangeable extraction and was found to have no influence on the subsequent acid extractable and iron and manganese oxides extractions. Removal of manganese oxides by the organic matter extraction was not thought to be significant since these only constituted two percent of the total iron and manganese oxides fraction. However, using a powerful oxidising reagent early in the extraction sequence is probably inadvisable as it could potentially alter other phases.

The iron and manganese oxides and the organic matter fractions are frequently ill defined, due to multiple coatings of iron oxides and organic matter. High iron concentrations in the organic matter fraction are caused by coatings of iron oxides on organic matter or by complexation of iron by organic matter (Maher, 1984). Conversely organic matter associated with iron oxides may be dissolved during the extraction of amorphous iron oxides.

There are a large number of problems associated with sequential extraction techniques (Calmano and Förstner 1983). The differentiation between sulphides and organic matter is difficult. Formation of metal hydrous oxides may occur if high pH extractants are used, particularly sodium hydroxide and sodium pyrophosphate. The reactions are influenced by pH, temperature, duration of the extraction and the ratio of extractant to substrate. Care must be taken to maintain the same conditions each time an extraction is carried out, to prevent experimental artefacts.

2.1.6 Metal Redistribution During the Sequential Extraction Procedure

The most serious criticism of sequential extraction techniques is the potential for metal extracted from one fraction to redistribute onto fractions that have not been extracted (Ajayi and Vanloon, 1989; Nirel and Morel, 1990). Investigating readsorption of heavy metals, onto other fractions, is very difficult (Tessier and Campbell, 1988). However, several studies have been undertaken, using three different approaches, to investigate the problem. Model sediments spiked with known concentrations of metals have been investigated by Kheboian and Bauer (1987) and Tipping et al. (1985). Standard additions of metals to extractants have been used in the extraction of natural sediments (Rendell et al., 1980; Beizile et al., 1989). In a study by Ajayi and Vanloon (1989), a natural sediment was spiked with a geochemical phase.

A comparison was then made between a sequential extraction carried out on this modified sediment and an unaltered control.

In a series of experiments by Rendell et al. (1980), uncontaminated sediments were shaken overnight, with an extractant that had been spiked with a known concentration of metal. By comparing the metal concentration in the extractant before and after the extraction, the metal that had been adsorbed could be determined. Readsorption of metals was found to occur with a number of extractants including: dilute hydrochloric acid, hydroxylamine hydrochloride and hydrogen peroxide. However, the study was not representative of the Tessier scheme in a number of ways. The extractants used all differed from those used in the standard Tessier scheme. For example, in the extraction of iron and manganese oxides, hydroxylamine hydrochloride was used without the 25% acetic acid buffer. The buffer is a critical component of the extraction holding the released metal in solution and thus preventing readsorption. The spiked metal concentrations were higher than would naturally be found in sediments for all heavy metals, and very much higher in the cases of lead and copper. Tessier and Campbell (1988) suggested that a similar study with more realistic spiked metal concentrations might show much lower percentage readsorption. A study of this type has been carried out on natural sediments using metal spikes that never exceeded the total concentration of the metal present in the natural sediment (Beizile et al. 1989). The study showed that readsorption had been overstated. Readsorption was not observed except in the case of lead in the acid extractable fraction. It was suggested that lead leached by the pH 5.0 buffered sodium acetate was desorbed from the surface of iron oxyhydroxides, as the sediments in this study were low in carbonates.

A study of a natural mixture of iron and manganese oxides, from a disused mine shaft, was made by Tipping et al. (1985), who compared a sequential extraction using hydroxylamine hydrochloride and ammonium oxalate, with electron microscopy and electron probe microanalysis. The hydroxylamine hydrochloride extractant was used without a buffer. Comparison of the two techniques showed that lead was redistributed from manganese oxides onto iron oxides, where it was extracted during the oxalate extraction. The authors explained the discrepancy by pointing out that the first extraction was sufficiently acidic to remove the lead from the manganese oxide, but sufficiently basic to allow it to be taken up on iron oxides. Their result confirms the importance of having a buffer in sequential extraction reagents to prevent, or at least to minimise, readsorption.

In a study of a model sediment doped with adsorbed or coprecipitated heavy metals, Kheboian and Bauer (1987) compared the Tessier sequential extraction scheme with X-ray diffraction and scanning electron microscopy. The model sediment consisted of four phases:

(i) Calcite doped with lead,

(ii) Humic acid doped with copper,

(iii) Iron sulphide doped with zinc,

(iv) Iron oxyhydroxide doped with copper and nickel.

Tessier and Campbell (1988) commented that this mixture is unrealistic, as recently formed iron sulphide and iron oxyhydroxide would not occur together in natural sediments. The study found redistribution of the metals, but this would be expected given that the model system had metals doped in phases where they would not normally occur in nature. An example of this is that copper bound in the iron oxyhydroxide phase redistributed onto the humic acid. Copper has a very strong affinity for humic acid, and in natural soils and sediments a large proportion of copper occurs in the organic phase.

Ajayi and Vanloon (1989), doped a real sediment with an additional synthetic phase and no redistribution of metals in the sediment was observed for cadmium, copper or nickel. Limited redistribution was observed for chromium, lead and zinc, in the iron and manganese oxides and organic phases, these results supported the work of Beizile et al. (1989).

The results of studies investigating redistribution of heavy metals in the Tessier sequential extraction scheme have been mixed. No study has shown conclusively that redistribution of heavy metals occurs in conditions analogous to those existing in the majority of natural soils and sediments. The use of doped phases in redistribution studies is problematic since it is difficult to prove that the model associations are comparable to those found in field soils and sediments.

2.2 Soil Chemical Properties and Parallel Extraction

Development of a Parallel Extraction Scheme

An alternative to extracting a sample sequentially with increasingly powerful reagents is to extract subsamples independently with different extractants. The results of the different extractions are compared, to determine the distribution of heavy metals between the fractions. Figure 2.2 illustrates the principles of this type of extraction scheme. Surprisingly few, if any, studies have adopted this approach. In some respects the scheme of McLaren and Crawford

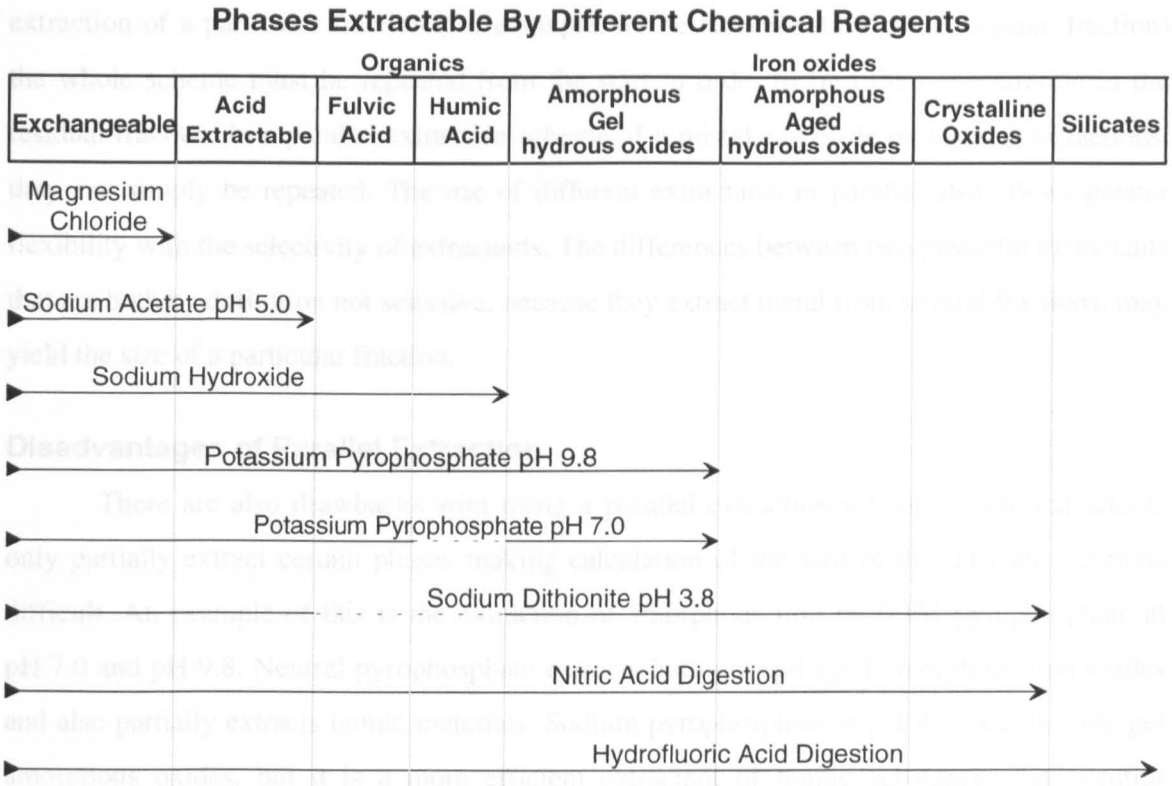


Figure 2.2 Based on Bascomb (1968)

(1972) is a parallel scheme. They determined copper bound to organic matter by using a 1.0M potassium pyrophosphate extraction, however, the extraction also removed exchangeable copper and copper bound by specific sorption. Exchangeable copper was determined separately by 0.05M calcium chloride extraction and specifically adsorbed copper was extracted by 2.5% acetic acid. They corrected the pyrophosphate extractable fraction, by the amount of copper in these fractions, to obtain a true value for organic matter bound copper.

Advantages of A Parallel Extraction Scheme

There are several advantages of using a scheme of this type. Some of the soil or sediment is lost during the physical processing of each step in the sequential extraction scheme, so that in the latter stages of a sequential extraction the amount of material being extracted may be much less than the one gram sample extracted during the first stage. As a result, the concentrations of heavy metals in the fraction will be underestimated and overall the results will be biased towards the more easily extractable fractions. In a parallel extraction scheme, each extraction is carried out on one gram of freshly weighed sample, there are no compound errors due to physical processing of the material. The sequential extraction scheme does not allow individual phases to be extracted in isolation. If a mistake is made during the

extraction of a particular fraction (for example, in the determination of the organic fraction) the whole scheme must be repeated from the start in order to find the concentration in the residual fraction. In a parallel extraction scheme, if a mistake is made on a set of extractions, they can simply be repeated. The use of different extractants in parallel also allows greater flexibility with the selectivity of extractants. The differences between two powerful extractants that are both by definition not selective, because they extract metal from several fractions, may yield the size of a particular fraction.

Disadvantages of Parallel Extraction

There are also drawbacks with using a parallel extraction scheme. Some extractants only partially extract certain phases making calculation of the size of the different fractions difficult. An example of this is the extraction of amorphous iron by 0.1M pyrophosphate at pH 7.0 and pH 9.8. Neutral pyrophosphate extracts both gel and aged amorphous iron oxides and also partially extracts humic materials. Sodium pyrophosphate at pH 9.8 extracts only gel amorphous oxides, but it is a more efficient extractant of humic substances than neutral sodium pyrophosphate. At face value it would appear that the gel and aged amorphous iron concentrations could be determined separately by calculating the difference between the iron concentrations in the two extractions. In practice, because different amounts of humic material are extracted by the two reagents, the result is inaccurate determinations of the gel and aged amorphous iron fractions. In fact, the situation is not quite as bad as it at first appears. For, if metals are associated with amorphous iron oxides at much higher concentrations than they are associated with humic substances, the error from the differences in the percentage of the humic substances extracted by the different reagents is small.

In some instances sequential extraction is tolerant of experimental error. If the initial amount of soil is weighed out incorrectly the absolute concentrations determined in a sequential extraction will be wrong. However, percentage distributions of metal between the phases will be unaffected. In a parallel extraction scheme this would not be the case, as each extraction is independent of the others. Differences in the amount of material used in a parallel extraction scheme will lead to errors in the calculated distribution of metals between phases.

Justification for Using the Parallel Extraction Scheme

One aim of the present study was to relate the results from a sequential extraction scheme to the soil composition and chemical properties, measured by standard soil science methods. Many of the techniques employed to measure soil properties involve the dissolution

of solid phases, for example, sodium pyrophosphate determinations of the amorphous iron oxides content of soils. It became apparent that the heavy metals associated with these phases are dissolved simultaneously. Heavy metals released by these extractions may then be determined by atomic absorption spectrophotometry.

The organic matter extraction and purification method, described in Chapter 3, has a large number of steps and is very time consuming. The use of a greatly simplified scheme reduces the accumulation of errors that are inevitable with complex schemes. To minimise cumulative errors the ideal chemical extraction method is to leach a soil sample with a single reagent. The solution may then be analysed after solid materials have been removed by centrifugation or filtration. The more steps used in the purification of the extractant, the more chance there is for errors to build up. Extracting humic substances by 0.1M or 0.5M sodium hydroxide does not remove heavy metals from amorphous iron oxide, or acid extractable phases. This enables the extraction to be used without the complex purification procedures needed to separate fulvic acid bound metals from other metals in the extractant solution.

2.3 Availability of Heavy Metals in Soils

Availability of the heavy metals in soils is commonly determined by chemical extraction using ammonium acetate or EDTA. In sequential extraction studies available metal is likely to include all of the exchangeable and acid extractable fractions, which are in effect ammonium acetate extractable. Sequential extractions should be better predictors of plant available heavy metals than total digestion, which does not distinguish between available and unavailable forms of heavy metals.

2.4 Fractionation of Heavy Metals In Soils And Sediments

Sequential extraction techniques have been used in many studies to estimate the geochemical fractionation of heavy metals in soils. Comparison of these studies is made very difficult by the wide variations in the extractants and conditions used in different sequential extraction schemes. There are two ways of characterising and comparing geochemical fractionation studies. One way is to compare studies by the type of input, such as sewage sludge application, aerial deposition or mine tailings. The other approach is to compare studies with the same type of system, for example, soils or sediments. This review compares estimates of the geochemical fractionation of heavy metals, determined by sequential extraction, in

groups of studies with similar heavy metal inputs to determine general patterns of metal speciation. The five phases extracted by the Tessier type sequential extraction schemes are:

(i) Exchange sites of minerals and organic matter on exchange sites,

(ii) Carbonates,

(iii) Iron and manganese oxides,

(iv) Organic matter,

(v) Silicates.

Sequential extraction schemes give the impression that metals can be partitioned accurately into single particular phases. Whilst it is useful to be able to describe a metal as being bound to a particular phase, with a few rare exceptions, it is an oversimplification of the real situation, which is extremely complex. Many soil components interact with heavy metals by several different mechanisms. Organic matter is an important source of exchange sites in soils and can also form chelation complexes with heavy metal ions, in both soil and water systems. Iron oxides are frequently associated with organic matter forming complex substrates. As a direct result of these properties, heavy metals associated with organic matter may be released in the exchangeable or organic phases, depending on the type of interaction between the metal and the organic molecules. To complicate the situation further, organic matter is a term that covers a whole range of organic molecules, discussed in Chapter 3, from discrete molecules of known composition to those of unknown structure including lignin and humic and fulvic acids.

Comparison of sequential extraction estimates of geochemical fractionation with determinations of important soil factors, greatly increases the value of the results. Soil properties such as pH, cation exchange capacity, organic matter concentration and composition are key factors determining the speciation of heavy metals in soils. Soil pH plays a major role in determining the geochemical fractionation of heavy metals in soils, due to competition between metal ions and hydrogen ions for various binding sites. Organic matter complexation of heavy metals, particularly by humic substances, is important to the speciation of heavy metals in soils and is described in detail in Section 3.3.

The chemical form of the heavy metal input is also important to its subsequent speciation in soils. The Tessier sequential extraction scheme was designed to investigate the speciation of heavy metals in sediments, where metals are frequently associated with sulphides and iron and manganese oxides. Many studies have investigated the geochemical fractionation

of heavy metals that enter the soil in the form of sewage sludge applications. These metals are likely to be soluble or associated with the organic compounds in the sewage sludge. Several studies have looked at heavy metals from industrial activity, including metal smelting, and their speciation in soils. The present review compares the geochemical fractionation of heavy metals in sewage sludge treated soils, sediments, street dusts and soils, to determine whether particular heavy metal associations with specific geochemical phases occur under a wide range of conditions.

2.4.1 Studies of Sewage Sludge Applications

There is a very large literature concerning sewage sludge applications to soils. This section will look at a few of the many studies that have used sequential extraction to estimate the partitioning of heavy metals in sewage sludge treated soils. Several studies have investigated the changes that may occur to the geochemical fractionation of heavy metals in soils during long term application of sewage sludge. These studies have been of considerable environmental interest resulting in recent American Environmental Protection Agency legislation and European Union directives limiting the application of sewage sludge to soils, when heavy metal concentrations reach a certain value. There is also concern over the potential for leaching of heavy metals into ground water and rivers.

Sims and Kline (1991) determined the geochemical fractionation of heavy metals, from the co-composting of sewage sludge and municipal waste and attempted to correlate the fractionation of these heavy metals with plant uptake. The study investigated Atlantic coastal soils amended at four rates with co-composted sewage sludge and examined the effect of liming on the heavy metal distributions in the soil. The liming of the soil produced a soil pH in excess of pH 6.5, however, changes in heavy metal distributions were found to be less than 5% for cadmium, chromium, nickel and lead. Application of lime to the soil was found to decrease the organic bound copper as extracted by sodium hydroxide. The authors concluded that the results of the study supported the premise that metals entering the soil in the sewage sludge revert to less available forms.

Long Term Studies of Sewage Sludge Application

A few studies have investigated the fate of heavy metals from long term sewage sludge applications (e.g. McGrath and Cegarra, 1992; Chang et al., 1984). McGrath and Cegarra (1992) investigated the geochemical fractionation of lead, zinc, cadmium, copper, nickel and

chromium after 19 years of sewage sludge or fertiliser application. The authors found that most of the changes in the geochemical fractionation of heavy metals occurred in the first 10 years of sewage sludge applications. In the following thirty years, including 20 years that occurred after applications of sewage sludge had ceased, little change was observed in the geochemical fractionation of heavy metals. Chang et al. (1984) studied the application of two liquid, and one composted, sewage sludges applied to 2 soils over a 7 year period. The soils were cropped with Barley, which was analysed for heavy metal content. The geochemical fractionation of the heavy metals, chromium, copper, nickel and zinc was determined every 4 weeks. Before the application of sewage sludge, the metals were mainly distributed in the acid extractable and sulphide-residue fractions. After the sludge application, copper, nickel and zinc were distributed between the acid extractable and organic phases. The geochemical distributions of chromium, cadmium and lead were unaffected by sewage sludge applications.

Availability of Heavy Metals Entering the Soil with Sewage Sludge

Chang et al. (1984) reported elevated concentrations of zinc and cadmium in barley plants grown on soils which had received sewage sludge applications. Sims and Kline (1991) found that sequential extraction results were a better predictor of heavy metal concentrations in plants than total digestion results. Using multiple regression statistical analysis, they demonstrated that soil metal fractions, pH and metal concentrations were significantly related to copper, zinc and nickel uptake in wheat and soybean plants. McGrath and Cegarra (1992) observed that, in order of relative abundance, the highest proportions of cadmium, zinc and nickel were present in the exchangeable phase after sewage sludge application. Lead was most abundant in the acid extractable fraction, whilst copper was shown to be mainly complexed with organic matter and chromium was found to occur mainly in the residual fraction. Campanella et al. (1987) studied the speciation of heavy metals in urban sludges by a series of chemical extractions and a sequential extraction scheme. They reported that manganese was mainly present in the form of soluble salts and was not extracted by alkaline extractants. Copper was shown to be extracted most effectively by basic solutions, implying an association with humic matter. The stability of humic complexes were in the order: copper >> zinc > manganese. Lake et al. (1984) reported that anaerobic conditions reduced the availability of the heavy metals cadmium, zinc and copper, and increased the availability of lead and chromium. Table 2.2 summarises the geochemical fractionation of heavy metals in sewage sludge amended soils.

Table 2.2: Summary of Sequential Extraction Results for Sludge Treated Soils

The principal associations of cadmium, lead, zinc, copper and nickel with the geochemical phases defined in the Tessier sequential extraction scheme. Where a different extraction scheme was used, the results are expressed in the equivalent Tessier fraction. The aim of the table is to list the main phase with which heavy metals were associated. The table is not intended to give an accurate account of heavy metal distributions in sludge treated soils, but to summarise the general trends observed.

Geochemical Fraction Sludge treated soils	*Main metal associated with Fraction*	*Source*
Exchangeable	Cadmium	McGrath (1992)
Acid Extractable	Lead, Zinc	McGrath (1992)
Iron and Manganese Oxides	Lead, Zinc	McGrath (1992)
Organic	Copper Copper, Nickel, Zinc Copper	Campanella et al. (1987) Chang et al.(1984) McGrath (1992)
Residual	-	-

2.4.2 Associations of Heavy Metals with Phases in Sediments

Studies of the geochemical fractionation of heavy metals in sediments have investigated their associations with the iron and manganese oxides fraction in considerable detail. The consideration of the behaviour of these phases in sediments provides a useful comparison with their behaviour in soils.

There are a number of the physical and chemical mechanisms that are important to the speciation of heavy metals in soils and sediments. Sorption of heavy metals to geochemical phases may take place by a number of different mechanisms including: physical forces, such as van der Waals forces; ion-dipole and dipole-dipole interactions (Calmano and Förstner, 1983). Chemical adsorption takes place when heavy metals form associations with the surface of a solid phase. Ion exchange may also take place where heavy metal ions substitute for other cations. Förstner (1982) reviewed the geochemical fractionation of heavy metals in lake sediments and suggested that clay minerals, carbonates and suspended materials form nucleation centres for the deposition of iron and manganese hydroxides. Acidification of lakes results in the release of zinc, cobalt and nickel from easily reducible sediment phases.

Carbonate precipitation results in the immobilisation of heavy metals and reduces the dissolved inputs of zinc and cadmium to lakes. It is also an important mechanism preventing

leaching of heavy metals into aquifers. The distribution of heavy metals in an alluvial aquifer has been studied by Polic and Pfendt (1994). The aquifer geology was found to act as a geochemical filter by the processes of adsorption, ion exchange and co-precipitation, which immobilised metals, preventing leaching. The authors suggested that changes in the pH or redox conditions of the aquifer could result in the mobilisation of heavy metals causing toxicity. Lion et al. (1982) reported the distribution of lead and cadmium in estuarine sediments in the south San Francisco bay harbour, using the Tessier extraction scheme and found that lead was mainly associated with the iron and manganese oxides phase, whereas cadmium was mainly associated with the organic phase.

Table 2.3: Summary of Sequential Extraction Results for Sediments

The table lists the principal associations of heavy metals with the geochemical phases found in sediments. It is clear from this table that copper tends to be associated with the organic and residual phases. Lead was primarily associated with the iron and manganese phase, zinc was mainly associated with the acid extractable and iron and manganese oxides phases and cadmium was associated with the acid extractable phase.

Geochemical Fraction Sediments	*Main metal associated with Fraction*	*Source*
Exchangeable	Very Low [HM]	Calmano and Förstner (1983)
Acid Extractable	Cadmium	Calmano and Förstner (1983)
	Cadmium	Gadh et al. (1993)
	Zinc	Calmano and Förstner (1983)
Iron and Manganese Oxides	Lead, Zinc	Calmano and Förstner (1983)
	Lead	Gadh et al. (1993)
	Lead	Lion et al. 1982)
	Lead	Rauret et al. (1988)
Organic	Copper	Calmano and Förstner (1983)
	Copper	Gadh et al. (1993)
	Copper	Rauret et al. (1988)
	Cadmium	Lion et al. (1982)
	Cadmium	Nair et al. (1991)
Residual	Copper, Lead	Calmano and Förstner (1983)

Speciation of Heavy Metals in River Sediments

Nair et al. (1991) investigated the speciation of heavy metals in river sediments of the Cochin estuary in southwest India. The aim of the study was to identify the geochemical phases important to metal speciation, using the Tessier scheme, and the anthropogenic sources

of the heavy metals. The study investigated sites along a transect down stream under both freshwater and estuarine conditions. The proportion of heavy metals in the iron and manganese oxides fraction was found to be relatively low and was similar at all the sites studied. Gadh et al. (1993) studied the distribution of cadmium, copper, lead and zinc in sediments of the Yamuna river, India, using the Tessier sequential extraction scheme. Cadmium was mainly associated with the acid extractable phase, whereas copper was strongly associated with the organic phase. A high proportion of lead was associated with the iron and manganese oxides fraction. Although this fraction was not considered to be available, the authors point out that the overall concentration of lead in the sediments was very high. While only a small proportion of lead was present in the exchangeable and acid extractable phases, the high overall concentration of lead means that the absolute concentrations in the available phases may be sufficient to constitute an environmental hazard. Rauret et al. (1988) reported the geochemical fractionation of copper and lead in a Mediterranean river sediment. Copper was associated with the residual and organic fractions and lead was associated with the iron and manganese oxides phase. The association of cadmium with the organic phase in some studies is surprising, given its relatively low affinity for organic matter (Stevenson, 1976). This may be attributed to the dissolution of cadmium associated with sulphide phases, which are extracted by the hydrogen peroxide reagent used in the Tessier sequential extraction scheme.

Suitability of Sequential Extraction for Different Metals

The Tessier sequential extraction scheme was developed, and has been used, mainly for the determination of the geochemical fractionation of lead, zinc, cadmium, copper and nickel. A few studies have investigated the speciation of other heavy metals using the Tessier scheme. Gruebel et al. (1988) tested a sequential extraction scheme for the extraction of arsenic and selenium, using similar reagents to those used in the Tessier scheme. The study looked at a model system, using freshly prepared goethite and amorphous iron oxide, together with a laboratory montmorillonite fraction. Hydroxylamine was found to dissolve amorphous iron with minimal dissolution of goethite, supporting the argument that hydroxylamine extracts metals associated with amorphous iron oxides. Therefore, in the Tessier scheme, metals bound in the lattice of crystalline iron oxides are released in the residual phase by concentrated acid digestion. The study showed that the action of hydrogen peroxide resulted in the oxidation of mineral bound selenium (IV) oxide to selenium (VI) oxide, which was released into solution. The net result was an overestimation of the size of the organic phase.

2.4.3 Heavy Metals in Urban Soils and Street Dusts

Urban soils, roadside soils and street dusts are a group of substrates where the main input of heavy metals is almost always aerial in origin. These substrates tend to be of relatively high pH, which has important implications for the speciation of heavy metals. Fergusson and Ryan (1984) investigated the sources of various elements in street dusts in two types of urban environment. Large cities, such as London and New York, were found to have very different elemental deposition to small cities, such as Christchurch, New Zealand; Halifax, Canada; and Kingston, Jamaica. The street dusts in large industrial cities were found to have high levels of calcium, cadmium, lead, chromium, zinc and copper, derived from vehicle tyre wear and exhaust emissions. The street dusts in small cities were found to have high concentrations of a different range of elements, aluminium, potassium and sodium amongst others. These elements were probably derived from soils in the surrounding areas. The results of studies investigating heavy metal speciation in roadside soils and street dusts are summarised in Table 2.4.

Hamilton et al. (1984) used the Tessier sequential extraction scheme to investigate the distribution of heavy metals in street dusts at three sites in outer London, each with different surfaces and traffic usage. The study showed that spatial variation of the dust loading was high, but the spatial variation of the heavy metal concentrations in the dust were low. The dusts were found to be of neutral pH. Hamilton et al. (1984) and Fergusson and Ryan (1984) reported that copper was mainly associated with the organic and residual phases in urban soils. Cadmium was most abundant in the acid extractable phase and zinc was most abundant in the iron and manganese oxides and acid extractable phases. The importance of the acid extractable phases was anticipated given the neutral pH of these substrates.

Harrison et al. (1981) applied the Tessier sequential extraction scheme to street dusts and roadside soils in Lancaster and London. The pH range of the dusts and soils examined was from pH 6.9 to pH 8.4. At these pH values, the carbonate phase becomes an important sink for heavy metals and lead and zinc were found to be predominantly associated with the acid extractable and reducible fractions. In two similar studies, Gibson and Farmer (1984; 1986) reported the results of the sequential extraction of heavy metals in street dirts and roadside soils in Glasgow. A variation of the Tessier sequential extraction scheme was employed, where the iron and manganese oxides phase was extracted with two reagents to obtain separate estimates of the easily and moderately reducible components. The easily reducible components were manganese oxides, whilst the moderately reducible components were almost

certainly amorphous iron oxides. The extractant used, hydroxylamine in 25% v/v acetic acid, was insufficiently powerful to extract crystalline iron oxides. Total concentrations of heavy metals in the soils and dirts were estimated by summing the fractions determined in the Tessier sequential extraction scheme. This estimation has the disadvantage that there were no independent total digestion results with which to check the results of the Tessier scheme by summing the Tessier fractions. Exchangeable metal was found to be higher in the street dust than in the roadside soil. This was also true of the combined exchangeable and acid extractable fractions, which corresponds to available metal. Lead was found to be most strongly associated with the acid extractable and moderately reducible fractions. Over 50% of lead in the roadside soil and 27% of lead in the street dust was associated with the amorphous iron oxides phase. Copper was mainly found in the organic and residual fractions, whilst zinc was fairly evenly distributed between the different fractions, with the highest concentrations of zinc occurring in the residual fraction. Very little if any of the heavy metals were found in the easily reducible fraction. Cadmium had the highest proportion of any metal in the exchangeable phase. Overall, the geochemical distributions of zinc and cadmium were similar, except in the exchangeable phase.

Table 2.4: Results of Sequential Extraction of Roadside Soils and Sediments

Geochemical Fraction Roadside soils	*Main metal associated with Fraction*	*Source*
Exchangeable	Cadmium	Harrison et al. (1981) Gibson and Farmer (1984) Gibson and Farmer (1986)
Acid Extractable Iron and Manganese Oxides	Cadmium, Lead, Zinc	Fergusson & Ryan (1984) Gibson and Farmer (1984) Gibson and Farmer (1986) Hamilton et al. (1984) Harrison et al. (1981)
Organic	Copper Copper Copper Copper and Lead	Gibson and Farmer (1984) Gibson and Farmer (1986) Harrison et al. (1981) Hamilton et al. (1984)
Residual	Copper, Zinc Copper, Zinc Copper Copper Copper	Gibson and Farmer (1984) Gibson and Farmer (1986) Fergusson & Ryan(1984) Harrison et al. (1981) Hamilton et al. (1984)

The bioavailability of lead in the Gibson and Farmer (1984) study was determined by an extraction using 0.07 molar hydrochloric acid. The aim of this extraction was to simulate the effects stomach acid digestion on ingested dust, to give an estimate of the potential risk to children. Harrison et al. (1981) estimated that the order of bioavailabiliy of heavy metals in roadside soils and dusts to be: cadmium > lead = zinc > copper. The mobility of the heavy metals was estimated in a later and extended study (Gibson and Farmer, 1986) to be in the order: cadmium >> lead > zinc > copper.

Heavy Metal Fractionation in Mine Tailings

The geochemical fractionation of heavy metals in lead-zinc mine tailings and waste from Leadville, Missouri, USA, were determined by Clevenger (1990), using the Tessier sequential extraction scheme with a nitric acid extraction to determine the residual fraction. The tailings were found to have high pH, owing to the presence of dolomite particles contained in the ore and were contaminated with cadmium and copper. Lead occurred in the iron and manganese oxides and residual fractions, while zinc was associated with the iron and manganese oxides and residual phases and was also present in the acid extractable phase. In contrast to the other studies reviewed here cadmium was mainly associated with the residual phase. The speciation patterns of lead, zinc and cadmium were somewhat different to those found in the other studies, reflecting the high pH of the mine tailings.

Laxen (1983) studied the adsorption and co-precipitation of heavy metals with hydrous iron oxides in a laboratory simulation. The results showed that co-precipitation with amorphous hydrous iron oxide resulted in a higher level of heavy metal uptake than adsorption. The authors suggested a mechanism where adsorption sites became blocked as the precipitate aged. The addition of humics to the solution enhanced the adsorption of lead, cadmium and nickel on hydrous iron oxides due to the formation of metal-humic complexes that have ligand like adsorption properties, with a negative surface charge, over a wide range of pH, enhancing metal associations. However, at pH 7 the adsorption of copper to hydrous iron oxides was found to be inversely related to the concentration of humic substances, due to competitive complexation. They suggested copper adsorption would be enhanced at lower pH.

2.4.4 Partitioning of Heavy Metals in Soils

Riise et al. (1994) conducted an experiment with radiolabled ^{109}Cd mixed with soil and sequentially extracted at regular intervals over a period of 221 days. Cadmium fractionation

was rapid during the first hour of contact with the soil. However, subsequent changes over the following 221 days were slow. They concluded that the initial reaction of cadmium with the soil was a rapid process, but the fixation of cadmium in soils was a very slow process.

The Effect of Total Metal Content and pH

Zhu and Alva (1993b) attempted to determine the effects of soil pH and total copper content on the partitioning of heavy metals, in the sandy soils of a citrus plantation in Florida, USA. Copper was the most abundant heavy metal, due to the application of copper fungicide. Lead and zinc were observed to be evenly distributed between the organic, precipitated and residual forms. Increasing pH resulted in an increase in the association of zinc and a decrease in the association of chromium and lead, with the organic matter phase. Soluble zinc and manganese decreased with increasing pH, due to increased precipitation. The percentage of copper found in the organic phase was inversely related to the total copper concentration in the soil, suggesting that at higher copper concentrations the organic matter binding sites became saturated and copper competed for adsorption sites on other phases.

Hickey and Kittrick (1984) sequentially extracted soils and sediments that were highly contaminated by metal smelting, or other industrial processes. They reported that copper was equally associated with the organic, residual and iron and manganese oxides fractions and that more than 50% of nickel was associated with the residual phase. Mclaren and Crawford (1972) studied copper speciation in soils and concluded that the bulk of the copper was bound to organic matter. They suggested that available copper was controlled by the equilibrium between specifically adsorbed copper and the soil solution. Cadmium was reported to have the highest association with the exchangeable phase, whilst zinc was principally associated with the acid extractable and oxide phases. Considerable concentrations of zinc were also present in the exchangeable phase. In a study of stabilised sands and marshes in the Donana National Park in Spain, Ramos et al. (1994) investigated the speciation of heavy metals by the use of a Tessier type sequential extraction scheme. Lead and zinc were found to be associated with the iron and manganese oxides fractions, while copper was found to occur in the organic and residual fractions. In the Hickey and Kittrick (1984) study copper was found to be associated with several phases, in contrast to most studies where copper is strongly associated with organic matter. The very high total concentrations of copper reported in their study suggest that the soil may have been saturated with copper so that the binding sites on organic matter were saturated and copper became associated with other fractions.

Table 2.5: Results of Sequential Extraction of Soils

Geochemical Fraction Soils	*Main metal associated with Fraction*	*Source*
Exchangeable	Cadmium	Ramos et al. (1994) Hickey and Kittrick (1984) Jeng and Singh (1993)
Acid Extractable	Cadmium Zinc	Ramos et al. (1994) Hickey and Kittrick (1984)
Iron and Manganese Oxides	Copper, Cadmium, Zinc	Hickey and Kittrick (1984)
Organic	Copper	Ramos et al. (1994) Hickey and Kittrick (1984) McLaren and Crawford (1972) Zhu and Alva (1993b)
Residual	Copper Copper, Nickel Zinc	Ramos et al. (1994) Hickey and Kittrick (1984) Jeng and Singh (1993)

Jeng and Singh (1993) studied the geochemical fractionation of cadmium and zinc in various sewage sludge treated cultivated soils in Norway. The samples were taken from the top 20cm of the soil profile and extracted by the Tessier sequential extraction method. Soil pH was found to be in a narrow range from 5.9 to 6.2. The results of the study showed that approximately 50% of cadmium was present in the exchangeable fraction, with another 30% of cadmium in the iron and manganese oxides phase. Ramos et al. (1994) reported similar results for cadmium which was highly bioavailable, occurring in the exchangeable and acid extractable phases. In the Jeng and Singh (1993) study zinc was shown to occur in the residual (50%) and iron and manganese oxides phase (30%). The authors comment that cadmium was weakly bound to organic matter and was easily displaced by the exchangeable extractant.

2.4.5 Conclusions: Geochemical Fractionation Studies

The results of the numerous sequential extraction studies carried out are surprisingly consistent, both within studies of similar systems and between studies of different substrates such as sediments and sewage sludge applications to soils. In just about every study reviewed copper was found to be associated with the organic and residual phases. The association of zinc varies slightly between the different studies, but the general pattern is for zinc to be found

in the acid extractable, iron and manganese oxides, and residual phases. Lead occurred mainly in the iron and manganese oxides fractions and cadmium was found to occur principally in the exchangeable and acid extractable fractions. At high soil pH values, cadmium tends to be present in the acid extractable phase, with some binding to organic matter. In acidic soils, cadmium tends to be associated with the exchangeable phase. Soil pH is clearly critical in determining the fractionation of heavy metals in soils. It is clear that the acid extractable phase is highly sensitive to pH, with high concentrations of metal occurring in the acid extractable phase only in neutral or alkaline soils. Acidic soils tend to have higher concentrations of exchangeable metal than neutral soils.

The effect of a single soil property on the speciation of heavy metals is difficult to determine, as the comparison of soils from different locations will inevitably mean a completely different set of soil properties, as well as different metal inputs and other environmental conditions. However, it is possible to investigate the geochemical fractionation of heavy metals at different depths in a single soil profile, in relation to the changes in soil composition and chemical properties that occur with increasing depth.

2.5 Down Profile Distribution and Fractionation of Heavy Metals

Dynamic Versus Static Approach to H.M. Speciation Studies

The aim of down profile studies is to give a more accurate representation of the behaviour of metals in soils than is possible by the determination of heavy metal concentrations in bulk samples. The term down profile is used here to describe a study where the soil is sampled and analysed at a number of different depths in a soil profile, so allowing a better understanding of the key factors controlling the distribution and speciation of metals in soils. These factors include:

(i) Changes in soil properties and composition with depth,

(ii) Rates of metal deposition on to the soil surface,

(iii) Total metal concentrations in the soil,

(iv) Time that the metal has been present in the soil,

(v) Competition between different metals for the binding sites on various substrates in the soil.

The study of the distribution of heavy metals between the various geochemical phases at different depths in a soil profile, allows a much better understanding of the behaviour of metals in the soil than could be established by the analysis of bulk samples. Studies of heavy metal mobility and transport from soils into ground water benefit from this methodology. The understanding of the availability of metals to plants is enhanced by a knowledge of heavy metal distributions and geochemical fractionation at different depths in the soil profile. Plant roots, including those of many crop plants, penetrate below the surface layers of the soil allowing uptake of metals from deeper in the soil profile.

Despite these advantages, the majority of studies of heavy metal pollution in soils have looked at the geochemical fractionation of metals in mixed samples, collected from a single depth in the soil. Surprisingly few studies have investigated the distribution and geochemical fractionation of heavy metals at different depths in a single soil profile (Ross, 1994b). Studies of the distribution of metals at different depths in the soil profile, which have looked at a number of different metal inputs and soil types, are reviewed in this section. The types of metal inputs that have been studied include: aerial inputs from industrial complexes, metal smelters and vehicle exhaust emissions, contamination from mine tailings as a result of the extraction of metal ores and sewage sludge application.

2.5.1 Techniques Used in Down Profile Studies

Several different laboratory techniques have been used to investigate metal distribution and speciation at different depths in a soil profile. Dowdy et al. (1991) used a 4M nitric acid extraction to determine the distribution of metals in a soil that had undergone sewage sludge application over a period of 14 years. Another study of sewage sludge application, by Williams et al. (1980), used nitric acid digestion, to measure total metals in soils that had received massive sewage sludge application over a period of three years, together with a DTPA extraction, to estimate available metals in the sewage sludge treated soils.

The geochemical fractionation of heavy metals at different depths in soil profiles may be determined by the use of sequential extraction techniques. Using sequential extraction allows the detection of changes in geochemical fractionation, that may have important implications for the mobility and availability of heavy metals in soils. However, none of these studies have used the Tessier sequential extraction scheme, which is the most rigorously tested and widely used scheme of this type. Different studies have used a variety of sequential extraction schemes making comparisons between studies very difficult and prone to error. In

studies by Miller et al. (1983) and Miller and Mcfee (1983) an eight step scheme was used to determine the geochemical fractionation of heavy metals in the top 2.5cm of the soil, accompanied by acid digestion of the soil samples from different depths. Both studies were conducted on undisturbed soils in the industrial region of north-western Indiana, USA. A five step sequential extraction scheme was carried out by Saha et al. (1991) on 12 Indian soils at 4 different depths. Griffin et al. (1989) investigated 6 marsh soils to a depth of 1m using a five step sequential extraction scheme together with a nitric acid digestion procedure. Two other studies reviewed here have used a series of soil extractions based on soil chemistry techniques. Whilst these studies are not sequential they attempt to determine the geochemical fractionation of heavy metals, at different depths in soil profiles. Levy et al. (1992) investigated the distribution of metals in soils contaminated by mine tailings. Scokart et al. (1983) investigated three soils profiles by means of acid digestion and an ammonium acetate estimation of exchangeable metals. Clearly there is considerable scope for further work in this area.

2.5.2 Mobility of Heavy Metals in Soil Profiles

Leaching Column Studies

Soil columns have been used to simulate the leaching of metals from sandy soils (Miller et al. 1983). The aim of the study was to determine the soil capacity and retention mechanisms for heavy metals in soils that had received metal contamination from industrial activity in north-western Indiana, USA. The samples analysed were sandy soils under oak vegetation with high organic matter and iron content, and low clay content. In the study, soil cores were extracted from the field and treated with aqueous solutions to simulate the rainfall received during a one year or ten year period. The leachate from the columns was analysed for the presence of the metals lead, zinc, cadmium and copper, by flame atomic absorption spectrophotometry. The results showed that metals were retained in the upper layers of the soil, complexed by organic matter. The near neutral soil pH also allowed the precipitation of hydroxy-carbonate phases. These two mechanisms immobilised the heavy metals in the upper layers of the soil profile. Heavy metal concentrations in the leachate from the columns were found to be below the detection limits for all metals in all cases. The authors suggested that at low to moderate levels of heavy metal contamination, soils are very effective at retaining metals and preventing leaching into the ground water, even in soils with relatively good drainage. However, they concluded that further inputs of heavy metals to the soil, or acid precipitation, could result in the leaching of metals from the soil profile.

In a study by Emmerich et al. (1982) soil columns were used to investigate the geochemical fractionation of heavy metals after leaching the soil columns with the equivalent of 5 meters of precipitation, using river water from the Colorado river. The soil columns were reconstructed from the top 15cm of a soil profile into which sewage sludge had been mixed. Mobility of heavy metals was low with metals remaining in the soil sludge layer. In the sewage sludge less than 36% of the heavy metals cadmium, zinc and nickel were found to be in the residual phase, whereas in the soil 65% of the zinc and nickel were associated with the residual phase. Comparison of the geochemical fractionation of the metals before and after leaching showed a gradual shift to residual forms for cadmium, zinc and nickel.

Leaching of Heavy Metals From the Soil Profile

Dowdy et al. (1991) studied the retention and mobility of cadmium, lead and zinc at 7 depths in a soil profile, after 14 years of massive sewage sludge applications, using a 4.0M nitric acid extraction to investigate the possibility of metal movement beyond the rooting zone. They showed that there was limited movement of cadmium and zinc out of the tillage zone and no evidence of any movement of copper. In a similar study Williams et al. (1980) investigated the mobility of heavy metals in a loam soil, of pH 5.2-5.6, after three years of massive sewage sludge application mixed into the top 20cm of the soil profile. Heavy metal mobility was limited, with cadmium moving less than 5cm and zinc and lead less than 10cm. No movement of copper was detected and heavy metal mobilisation was restricted to the top 30cm of the soil profile.

Transport Mechanisms

The effect of seasonal desiccation of a soil profile, resulting in cracking at the base of the tillage zone during the growing season, on heavy metal mobility was investigated by Dowdy et al. (1991). They suggested that high levels of precipitation at other times of the year could result in water movement through the soil macropores generated by the drying cycle, leading to transport of ionised and organic matter chelated heavy metals. The results implied that heavy metal transport can be brought about by a combination of physical and chemical processes. In a study of soils contaminated by mine tailings, Levy et al. (1992) investigated pollution of montane meadows at a site near Leadville, Colorado, USA. Contamination of the soil was found to be caused by a combination of the direct deposition of mine tailings and application of contaminated irrigation water. Drainage of surface water through mine tailings was thought to cause transport of metals away from the physical location of the mine tailings.

Mobility of Aerial Inputs of Heavy Metals in Soil Profiles

The mobility of heavy metals in an acidic podzol and a neutral brown earth, within the vicinity of two zinc smelters in Belgium, was investigated by Scokart et al. (1983), in relation to soil properties and mineral composition. They reported that smelting had taken place at the site for over 50 years. Seven profiles of the podzol, with an average soil pH of 4.0, and 9 profiles of the neutral loam soil were examined, at a number of depths in the soil profiles. The accumulation of cadmium and zinc in the brown earth soils was up to 100 times greater than in the podzol soils, but accumulation of lead and zinc was similar in both soil types. The sandy podzols showed little accumulation of heavy metals and heavy metal mobility was associated with organic matter migration. However, some immobilisation of cadmium and zinc by organic matter complexation was detected in the podzol accumulation zone. In loam soils heavy metal mobility was strongly pH dependent, cadmium was found to become mobile when the pH of the soil was below pH 6, zinc became mobile only when the pH dropped below pH 5. The results demonstrated the importance of soil properties, particularly pH, on heavy metal speciation in soil profiles. Griffin et al. (1989), in an investigation of the geochemical fractionation of heavy metals in marsh soils found very different results for lead which was weakly complexed with organic matter and by implication readily mobile. The differences between the results of these two studies were almost certainly due to differences in the soil types. The tidal marsh soils investigated by Griffin et al. (1989) were completely different in terms of hydrology and redox conditions from the podzols and brown earths examined by Scokart et al. (1983). Organic matter was an important component in the mobilisation and immobilisation of heavy metals in both the soil types examined.

2.5.3 Geochemical Fractionation of Heavy Metals Down Profile

The following section reviews the general trends in the geochemical fractionation of heavy metals at different depths in soil profiles. The different types of ecosystems and metal inputs in the studies makes these comparisons very difficult, since there are a large number of environmental and edaphic factors that could account for variation in the geochemical fractionation of heavy metals. To clarify the findings of the studies reviewed, the metals have been considered separately where possible.

Copper

The most consistent results obtained in the various studies of geochemical fractionation down the soil profile are for copper. It has a high affinity for humic substances

and is usually found in the organic phase at all depths in the soil profile. Levy et al. (1992) reported that copper was mainly associated with the organic fraction, but iron oxide was also an important phase in the speciation of copper in some soils. Similar results were obtained by Saha et al. (1991). They observed that copper was mainly complexed with organic matter, but was also associated with the amorphous and crystalline iron phases. The exchangeable and manganese oxide phases increased in significance with depth in the soil profile, the result of decreasing organic matter concentration with depth, but they were not important geochemical phases for copper speciation. Griffin et al. (1989) reported that copper was predominantly associated with the organic matter and sulphide phases. This result was not surprising given the high organic matter and sulphide content of the marsh soils and sediments studied. By analysing soil samples from the top 2.5cm of a column leaching experiment, Miller et al. (1983) showed that a high proportion of copper was organically bound, while amorphous iron and manganese oxides were also shown to be important phases for copper fractionation. Similar results were observed during a study of the distribution of metals in soils in northwest Indiana, USA (Miller and McFee, 1983). The results of these studies indicated that in soils where high levels of metal contamination occurred, copper could also become associated with the acid extractable phase, probably due to organic matter binding sites becoming filled. Unfortunately because the sequential extraction scheme was only carried out on the top 0-2.5cm layer of the soil, the changes in geochemical fractionation of metals at different depths in the soil were not described. The surprisingly close agreement between these studies reinforces the evidence that copper has a very high affinity for the soil organic matter.

Lead

Levy et al. (1992) found lead mainly bound to the iron and manganese phase at all depths and locations, but lead was also complexed with organic matter. Griffin et al. (1989) reported that lead was weakly complexed to organic matter. In the Miller and McFee (1983) study lead was mainly associated with the occluded iron oxide and organic matter phases. Addition of lead in the solutions used in the soil column leaching experiments by Miller et al. (1983) resulted in the precipitation of lead with the carbonates and adsorption of lead on amorphous iron oxides.

Zinc and Cadmium

Zinc and cadmium have been found to be mainly associated with the iron and manganese oxides phase (Levy et al. 1992). They also reported that in the top layers of two

sites, which had high organic matter concentrations, zinc was strongly associated with the organic matter phase. Miller and Mcfee (1983) reported that in the top 0-2.5cm of the soil zinc was associated with the organic and iron and manganese oxides phases, while cadmium was associated with the exchangeable fraction. However, Griffin et al. (1989) found that zinc was mainly associated with the organic and sulphide occluded phases, a reflection of the reducing conditions of some of the marsh soils and sediments examined in the study. Cadmium exhibited similar properties to zinc and occurred as cadmium sulphide or was associated with organic matter.

2.5.4 Soil Properties and Heavy Metal Fractionation

The two soil properties most important to the geochemical fractionation of metals are:

(i) pH,

(ii) cation exchange capacity.

Soil pH is a key factor determining the geochemical fractionation of metals in soils at different depths in the soil profile. As pH becomes more acidic, heavy metals become increasingly mobile. Clay minerals and organic matter provide exchange sites which can bind heavy metals. Redox properties influence the behaviour of iron oxides and their associations with heavy metals in soils. Organic matter complexation and chelation are important controls on metal mobility, particularly copper, and are highly dependent on pH. Heavy metal binding to organic matter is discussed in Chapter 3.

Copper in the exchangeable fraction has been reported to be strongly correlated with pH (Saha et al., 1991). Cation exchange capacity would be expected to be strongly correlated with exchangeable metal but there is little if any evidence in the literature. Similarly, high pH has been associated with high levels of metal adsorption and low pH was associated with metal mobility (Miller et al., 1983).

Sewage sludge application has been shown to increase the acidity of the soil (Dowdy et al, 1991; Williams et al., 1980). Intensive application of sewage sludge over a 14 year period has been shown to result in a decrease in the soil pH of 0.6-0.9 units (Dowdy et al., 1991). The translocation of organic acids was thought to be the cause of this pH reduction.

Differences in the chemical properties and composition of different soil types have a major impact on metal speciation in soils. Scokart et al. (1983) suggested that in an acid podzol pH controls the mobility and organic matter governs the availability of heavy metals in the soil profile. Cation exchange capacity in loam soils was approximately constant with depth

in the soil profile. They found that at the top of the loam soil profile, organic matter was the main component contributing to cation exchange capacity. At lower depths in the soil profile, clay minerals provided most of the exchange sites, as organic matter concentrations decreased with depth. In the acidic podzol, organic matter content was found to decrease down the soil profile with a corresponding decrease in cation exchange capacity. The lack of an appreciable clay mineral or iron and manganese oxides fraction prevented much accumulation of heavy metals in the acid podzol soils examined in the study. In the loam soil, at the top of the soil profile, the influence of pH on the formation of precipitates with carbonates and phosphates controls the mobility of zinc and cadmium. At lower depths in the loam soil profile, amorphous iron and manganese oxides and clay minerals were the main factors controlling heavy metal availability and mobility. These soil components acted as a sink for heavy metals. In general the availability of heavy metals, determined by ammonium acetate extraction, was found to be lower in the loam soils than in the podzols. The pH dependence of cadmium and zinc mobility in loam soils was a result of the formation of carbonate and phosphate precipitates that controls metal solubility.

In marsh soil the bacterial reduction of sulphate to sulphide in a tidal environment is probably an important influence on metal speciation in those soils and iron was found to cycle between oxide and sulphide forms in the marsh soils examined by Griffin et al. (1989).

2.5.5 Conclusions

There is a trade off between the leaching of heavy metals from a soil profile and the accumulation of metal contamination in the upper layers of the soil. Soils that retain metals strongly prevent leaching of the metals into ground water and aquifers. Continued addition of heavy metal inputs may raise the metal concentration level to a point where all the binding sites are saturated. At this point further addition of metals will result in leaching of metal from the soil profile. If a soil has a low capacity for metal retention, then metals will be leached into the subsoil at a much lower metal loading than would be the case for a soil with a high capacity for metals.

The study of metal distributions at different depths in the soil profile provides much better information on the chemical forms and potential mobility of heavy metals in soils. Studies of the availability of metals to plants benefit from a knowledge of the chemical forms of heavy metals at different depths in the soil profile. The influence of soil chemical properties on the geochemical fractionation of heavy metals in soil profiles improves understanding of the factors controlling the availability and mobility of these metals. Such information may ultimately allow prediction of metal leaching from soil profiles into ground water.

3 Soil Organic Matter And Heavy Metals

3.1 Soil Organic Matter

Soils may have an organic matter content of between 0.1 and 100%, but typical agricultural soils contain between 1 and 5% organic matter in the top 0-15cm of the soil. Soil organic matter is an important soil component in relation to the geochemical fractionation of heavy metals since it performs a dual role complexing metals in both mobile and immobile forms. The importance of soil organic matter in metal complexation is not that it complexes large proportions of the total metal in the soil, although in some instances this may be the case, but that it acts as an important control on metal availability in the soil.

Soil organic matter may be divided into two categories:

(i) Humic substances,

(ii) Nonhumic substances.

Nonhumic substances are the minor constituent accounting for between 25 and 35% of the soil organic matter. They are characterised as having recognisable physical and chemical characteristics. It has been estimated (Schnitzer 1991) that approximately 10% of soil organic matter is in the form of carbohydrates, a further 10% is in the form of nitrogen containing compounds including amino acids, purines, pyrimidines and proteins. The remaining nonhumic compounds include alkanes, fatty acids, resins and waxes. Nonhumic substances are usually readily decomposed by soil micro-organisms and as a consequence they have a rapid turnover in the soil, measured in days rather than years. Nonhumic substances are important in the uptake of trace metals by plants, fungi and microorganisms. Plants produce root exudates, both simple and complex organic acids, that assist in the uptake of micronutrients. These organic acids include, aliphatic, amino and aromatic acids (Zunino and Martin, 1977).

Humic substances account for the remaining 65 to 75% of soil organic matter. They form a very large group of compounds with molecular weights ranging from a few hundred to a few thousand daltons. Humic substances are amorphous and tend to be dark coloured. The chemical properties vary within the group of molecules, they tend to be acidic and hydrophilic with varying degrees of aromatic character. To aid discussion of humic substances, which are an extremely diverse group of organic molecules, soil chemists have divided them into three classes, fulvic acids, humic acids and humin, depending on their solubility in acidic and alkaline solution and their molecular weight. The molecular weights of fulvic acids range from 500 to 2000 daltons, they are soluble in both acid and alkaline solutions (Schnitzer and Khan 1972).

Humic acids have molecular weights in the range 2000 to 10000 daltons, they are soluble in neutral and alkaline solutions, but insoluble in acid (Wershaw et al. 1990). Humin is the most difficult of the three substances to study, as it is insoluble in both acidic and alkaline solutions and different methods of extraction and fractionation are needed to isolate it from soils. These types of humic substances are, in reality, convenient labels for a wide range of very large and complex molecules that overall possess similar properties. The properties of humic and fulvic acids depend on their chemical composition, in particular the types and number of functional groups present on the molecule. In general fulvic acids are more highly oxided than humic acids with a higher proportion of oxygen containing functional groups, such as carboxylic acid and phenolic (Schnitzer, 1969; Schnitzer et al., 1981).

Humic compounds are highly resistant to degradation and have residence times in the soil of hundreds or thousands of years (Haider and Martin, 1987). The stability of humic acids in soils makes them an important sink for heavy metals. Humic acids are stabilised against decomposition by their complex structure, the formation of aggregates and their chemical associations with metal ions and clays. In fresh water, where these mechanisms are less significant, the residence times of humic and fulvic acids have been found to be much shorter, in most cases less than 20 years (Malcolm, 1985).

Formation of Humic Substances

There are two possible humification processes resulting in the formation of humic substances. The first process is degradative, where decomposition of molecules including waxes, lignins and other macromolecules from decomposing plants leads to the formation of humic substances. Lignin is thought to be one of the main precursors of humic and fulvic acids, however, the chemical composition and breakdown products of lignin are unknown in detail. The second process is the synthesis of humic substances from the reaction of the products of protein decomposition, amino acids and peptides with sugars (Hayes, 1991). Addition of organic matter and urea fertiliser to soils with a low humic content has been carried out to study the formation of humic substances (Amalfitano et al. 1992). Chemical modification of lignin in soils resulted in the formation of humic acids over a 1 year period.

3.2 Heavy Metal Associations with Soil Organic Matter

Studies of forest soils have shown that lead concentrations are highest in the older plantations, due to foliar interception of the metals (Billet et al., 1992). The effect of canopy type on organic matter interactions with heavy metals has been studied by Candler (1992). The

study compared the complexes of heavy metals with soil organic matter under birch and aspen canopies, by means of gel permeation chromatography and thin layer chromatography. The organics extracted under the different canopies were found to vary significantly with vegetation type. Manganese was shown to be weakly bound to organic matter. The study suggested the existence of vegetation type specific complexes of heavy metals with organic matter. The influence of vegetation on heavy metal binding at different pH values was also studied by Krosshavn et al. (1993). Soil samples were treated with solutions containing known concentrations of cadmium, copper, zinc and lead. The binding of copper and lead with soil organic matter was shown to be stronger than that of cadmium and zinc. The soil pH was found to have a greater influence on cadmium and zinc than on copper or lead. The treatment of samples after collection, drying at 35°C or 100°C and storage for three months, was found to have little effect on the metal binding capacity. The type of vegetation appeared to have an influence on the binding of cadmium, copper, lead, and zinc in the organic soils.

Organic matter content and pH are important controls on the accumulation or leaching of heavy metals from soils. The speciation of cadmium in the soil solution was studied by Hirsch and Banin (1990) in soils from an arid forest zone in Israel. Destruction of organic matter ligands by ultraviolet light showed that soil organic matter complexed cadmium was not an important component in the speciation of cadmium in the soil solution. The association of lead with soil organic matter has been found to be stronger at higher values of pH (Gregson and Alloway, 1984). In a study of the speciation of cadmium and lead in the soil solution, Tills and Alloway (1983) showed that only about 5% of cadmium metal was complexed with organic matter. These studies are in agreement with investigations of the sequential extraction of heavy metals in soils which usually show cadmium to be principally associated with the exchangeable phases and weakly associated with the organic matter phase.

Heavy metals have been shown to have significant effects on soil processes. In a study of lead and zinc contaminated pastures, McNeilly (1984) observed that high concentrations of lead resulted in a decrease in productivity and organic matter decomposition. The result was accumulation of litter due to inhibited humus decomposition.

3.3 Complexation of Heavy Metals With Organic Matter

Heavy metals may be associated with the functional groups of organic matter by three different mechanisms (Senesi, 1992; Hayes, 1991). The heavy metal ions form cation exchange complexes. Outer sphere complexation occurs when heavy metal ions are electrostatically

associated with the functional groups of humic substances and the metal and ligand remain in a hydrated form. Outer sphere bonding is the main mechanism by which the alkaline metals, calcium and magnesium are associated with organic molecules. Inner sphere complexation results in the formation of chelates, where a chelate refers to a complex in which the metal ion is bonded to a ligand by two or more bonds. The presence of two or more bonds results in a much more stable complex. The bonding in inner sphere complexation is covalent with the functional group donating one or more electron pairs to the metal ion. The formation of a chelate results in dehydration of the ligand and the metal ion which reduces their solubility.

There are two ways that a metal ion may form a chelate. The metal may form a single bond with two separate organic molecules forming a bridge. When a ligand has two potential adjacent binding sites the metal ion may form bonds with each site. In an aliphatic molecule this may take the form of two adjacent carboxylic acid groups. Figure 3.1 illustrates two arrangements of functional groups on an aromatic organic molecule. The phthalic acid type consists of two carboxylic acid groups on a benzene ring. The salicylate type has a phenolic group and a carboxylic acid group on the benzene ring. These structures have been observed by infrared spectroscopy (Stevenson and Goh, 1974).

Two other types of complexing functional groups are thought to be important in the complexation of heavy metals. The nitrogen containing amine and amino groups and the sulphur containing sulphydril, sulphide, disulphide and thioether functional groups. The functional groups have been classified (Senesi, 1992) by their preference for class A, class B and intermediate metals using the metal classification of Nieboer and Richardson (1980), see Section 1.3. The problem of such classification schemes is that they were not designed for

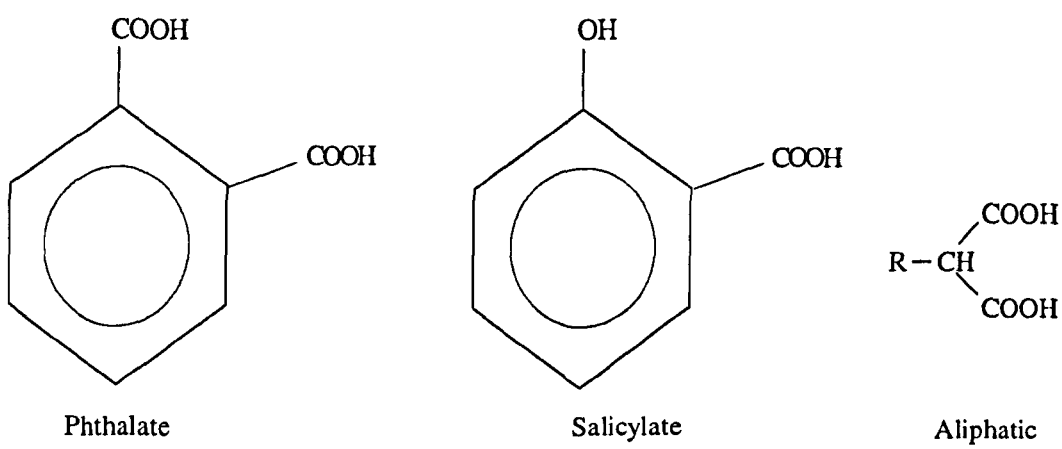


Figure 3.1 Functional Group Configurations in humic substances. Based on Ross 89

very large humic molecules, where the charge distribution around the functional groups is more complicated.

Stability of Humic and Fulvic Acid Complexes with Heavy Metals

Potentiometric titration has been used to determine the stability of heavy metal complexes with humic substances. A number of studies of the reactions of humic substances and heavy metals have been carried out. Schnitzer and Skinner (1963) investigated the reactions of organic matter extracted from a podzol with the various metal ions, by means of potentiometric and conductiometric titrations. The results of the Schnitzer and Skinner study showed that the solubility of the metal-organic complex decreased with the ratio of metal to organic matter. An order of complex stability was determined by Schnitzer and Skinner (1967). There was a slight difference in the order of stability of the complexes of heavy metals with organic matter at the two different pH levels studied.

pH 3.5 Cu > Fe(II) > Ni > Pb > Co > Ca > Zn > Mn > Mg

pH 5.0 Cu > Pb > Fe > Ni > Mn = Co > Ca > Zn > Mg

A similar study was performed using fulvic acid extracted from a podzol (Schnitzer, 1969) at two different pH levels. The results are listed below:

pH 3.5 Cu > Fe > Ni > Pb > Co > Ca > Zn > Mn > Mg

pH 5.0 Cu > Pb > Fe > Ni > Mn > Co > Ca > Zn > Mg

Copper clearly forms strong complexes with humic and fulvic acids. The results suggest that iron, lead and nickel also form strong complexes with organic matter. Zinc forms much weaker complexes and the alkaline metals, calcium and manganese form very weak complexes with humic substances.

The stability of lead, zinc, cadmium and copper complexes with humic acids has been determined (Stevenson, 1976; 1977). The results showed that copper complexes were the most stable, followed by lead. Cadmium complexes were found to be slightly more stable than those of zinc. Stevenson (1977) concluded that copper and lead formed inner sphere complexes, which he defined as 1:2 complexes, and cadmium and zinc formed outer sphere complexes, which he defined as 1:1 complexes. High affinities of zinc for fulvic acid type polymers have been observed at very low metal concentrations (Zuninio et al., 1979). Metal complexes with divalent metal ions were found to be soluble at low ratios of metal : humic acid, due to the formation of inner sphere complexes leading to a net charge on the molecule resulting in increased solubility.

Models of Heavy Metal Interactions with Humic Substances

Three main approaches have been used to model the binding of heavy metals to humic and fulvic acids:

(i) models with discrete binding sites,

(ii) models using continuous charge distributions,

(iii) statistical models.

Multi-site models are based on a number of discrete binding sites, whilst continuous stability function models attempt to use a function to describe the electrostatic charge distribution on humic substances. Most models are based on the results of potentiometric titrations used to investigate the binding of heavy metals with humic substances.

Discrete Binding Models identify a small number of discrete binding sites, usually 2 or 3. The binding sites are normally carboxylic acid or phenolic functional groups with heavy metal complexation taking place by proton dissociation. Discrete ligand models are not unique descriptions of heavy metal binding to humic substances. The discrete ligand model of Hering and Morel (1988) was successful at predicting the binding of calcium or copper with the humic acid, but the competitive effects predicted by the model were not observed.

Continuous function models are thermodynamic models solving the non-linear Poisson-Boltzmann equation, which describes the charge distribution around the humic macromolecule (Stevenson, 1991). The models often assume that molecules are impenetrable spheres. Bartschat et al. (1992) describe an oligoelectrolyte model used to explain the potentiometric titration results for the competitive complexation of copper and calcium.

In an attempt to overcome the problem of the chemical variability of fulvic acids, which is a major problem in the study of metal binding sites, statistical models of fulvic acids have been developed (Linder and Murray, 1987). By randomising the positions of aromatic rings and functional groups, possible binding sites of fulvic acids have been explored. Input parameters to these types of model include, elemental composition, percentage aromaticity and molecular weight. The models describe the binding capacity and stability constants for mono-, bi- and tri- dendate binding sites. Differences between fulvic acid properties tend to be small, fulvic acids differ mainly in aromaticity and the number of functional groups.

Competition of Metals for Binding Sites in Humic and Fulvic Acids

The competition of copper with the divalent cations magnesium and calcium has been studied at different pH values. The competition of copper and calcium for binding sites on

humic acids has been investigated by potentiometric titrations (Hering and Morel, 1988). The results for single metals were shown to be consistent with the predictions of a discrete ligand site model. The competitive effects predicted by the model were not observed when copper was used with excess calcium. In a study using the technique of synchronous fluorescence spectroscopy, Cabaniss (1992) observed that the presence of magnesium, at concentrations 1000 times higher than those of copper, had little effect on copper binding with fulvic acids at pH 5 or pH 7.5. However, the study found that aluminium ions were able to compete with copper for binding sites in fulvic acids. The results of these experiments suggest that there are different binding mechanisms for transition metals and alkaline earth metals.

The most important soil property controlling the complexation of heavy metals with organic matter is pH. Several studies have investigated the binding of heavy metals with humic substances at different pH values. Copper binding by coal derived humic acids in the pH range pH 1-3 was determined by Green and Manahan, (1977). The study found that copper ions were bound by humic acids at pH values down to 1.35. Two mechanisms of copper binding were suggested as explaining the behaviour of copper and humic acids. At high copper concentration and higher pH values hydrogen exchange binding of copper took place. Non-exchange bonding of copper occurred at all pH values, but assumed a greater importance under low pH conditions, as such bonding was by an inner sphere mechanism. Ram and Verloo (1985) studied the binding of lead, zinc, cadmium and copper to organic materials added to soil. The experiment was carried out over a wide range of pH. Over 95 to 97% of copper and lead were found to be retained in the soil when the pH was greater than 2. However, when the pH was reduced below 2, the lowest value used was pH 0.5, there was a 10 to 25 fold increase in mobile lead and copper. The increased mobility of lead and copper was attributed to hydrolytic decomposition of the very stable organic matter complexes. Both cadmium and zinc were solubilised above pH 2.

The studies of single metal binding to humic and fulvic acids have shown that most multi-valent metals will form inner sphere complexes with humic substances. In soils there are a number of metal ions competing for binding sites on organic matter and other substrates. The metals that have a high affinity for humic and fulvic acids will form inner sphere complex in preference to metals with a low affinity (Senesi, 1992). The outer sphere complexes are then formed by the metals with a lower affinity for organic matter. Organic matter is known to be a major contributor to cation exchange capacity and these metals will be released in the

exchangeable fraction of the Tessier sequential extraction scheme together with metals associated with the soluble fulvic acid fraction.

3.4 Soil Organic Matter Extraction Schemes

3.4.1 Principles of Soil Organic Matter Extraction

Techniques have been developed for the extraction of soil organic matter, especially for structural studies of the humic and fulvic acids components of organic matter. A major aim of soil organic matter extraction techniques is to maintain the structural integrity of the organic matter components. The present study investigated heavy metal binding to humic and fulvic acids in soils. Changes in the structure of the organic matter are likely to alter the binding of heavy metals to organic compounds, due to changes in the functional groups. It is for this reason that the same criteria used for structural studies of organic matter may also be used for studies of heavy metal binding to organic matter. There are three important criteria that have been used for the soil organic matter extraction methods intended to investigate the structure of humic and fulvic acids:

(i) the method should completely extract the organic matter representing all the fractions across the molecular range,

(ii) organic matter so extracted needs to be free of contaminants,

(iii) the method should be applicable to all soils to allow comparison between different soil types at the same or different locations.

These criteria apply equally well to the application of soil organic matter extraction techniques to the study of heavy metal association with humic substances. No single extraction method completely fulfils these criteria. A very wide range of extraction methods have been developed, partly depending on what properties of the organic matter were being studied. The extraction methods can be divided into two main categories, extraction schemes using inorganic extractants and schemes using organic solvents.

The following sections review the chemical principles, outline a representative scheme, and summarise the development and variations of organic matter extraction schemes. The methods used in the present study and the rationale behind them are then described.

Chemistry of Soil Organic Matter Extraction

The basis of soil organic matter extraction is the dissolution of humic substances by means of a dilute base extractant or organic solvent. In soils, the positive charges of divalent and polyvalent metal ions balance the negative charges of the conjugated bases in the acid groups of humic substances. The metal ions, such as calcium, iron and aluminium, act as bridges between humic strands and other humic strands or colloids (Schnitzer and Schuppli, 1989a). Inorganic extraction of humic substances relies on the replacement of the divalent and polyvalent cations with monovalent cations, releasing the humic substances into solution. Sodium pyrophosphate acts in precisely this manner. The pyrophosphate forms complexes or precipitates with these metallic ions, releasing the organic matter which is solubilised as a sodium salt (Schnitzer, 1982). The process may be summarised in an equation (Schnitzer, 1982; Alexandrova, 1960).

$$R(COO)_4Ca + Na_4P_2O_7 \quad \text{-->} \quad \underset{\text{Soluble}}{R(COONa)_4} + Ca_2P_2O_7$$

The acidic groups in humic substances become ionised as the pH of the medium is raised, the strongest acid groups are ionised first at relatively low pH, the weakest acid groups are ionised last at a much higher pH. The increasing ionisation of the humic substances allows them to overcome the intra- and inter- molecular hydrogen bonding that makes them relatively insoluble in water allowing dissolution to take place (Hayes, 1991). Sodium hydroxide is an effective inorganic extractant of humic substances. It is more alkaline than sodium pyrophosphate and in that sense it is a more effective solvent for organic substances.

3.4.2 Inorganic Extraction of Soil Organic Matter

Outline of Inorganic Extraction Procedure

The extraction of soil organic matter, by leaching the soil with dilute alkali, is illustrated in Figure 3.2. The extraction results in the dissolution of humic substances whilst clay mineral and other insoluble materials are held in suspension. The insoluble material including humin, the insoluble humic component, is removed by a physical process such as centrifugation or filtration. The humic and fulvic acid components are then separated by acidification of the solution to pH 2. Humic acid, which is insoluble in acidic solution, is precipitated forming an aggregate which may be removed from the solution by centrifugation, while fulvic acid remains in solution. The humic acid and fulvic acids are then purified to

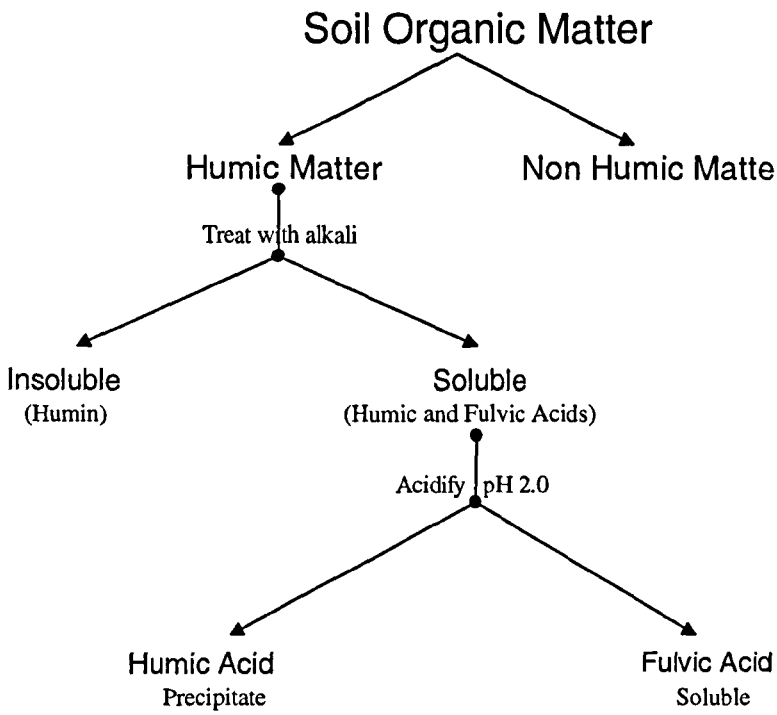


Figure 3.2 Fractionation of Humic Substances, based on Schnitzer (1982)

remove contaminants. The purification of humic and fulvic acids is discussed in detail in the next section.

The most frequently used inorganic extractants are sodium hydroxide and sodium pyrophosphate (Schnitzer, 1982). The first recorded use of sodium hydroxide was by a chemist called Achard in 1796, but it is still widely used today because it is the most efficient extractant for organic matter (Schnitzer, 1991).

Several slightly different procedures were used to extract and fractionate organic matter from soils during the course of these studies. The main reasons for changing the procedure were to:

(i) reduce the time required to extract the humic and fulvic acids,

(ii) increase the number of samples that could be processed at once,

(iii) improve the repeatability of the method.

The alterations were designed to allow more samples to be analysed improving the replication in the study. The variations between different schemes are discussed in the next section. The following procedure is based on that proposed by Schnitzer and Schuppli (1989a) and gives an outline of the extraction scheme. It is followed by a review of the differences in the schemes used by various researchers.

Procedure for Inorganic Extraction of Organic Matter

In the method used by Schnitzer and Schuppli (1989a) 30g of soil was weighed into a two litre polyethylene container. Three hundred millilitres of either 0.1M sodium hydroxide or 0.1M sodium pyrophosphate extractant solution were added to the soil. Before the extraction vessel was stoppered the air in the vessel was displaced by nitrogen to give an oxygen free atmosphere to avoid potential oxidation problems. The vessel was shaken for 24 hours on a reciprocal shaker. The supernatant was separated by centrifugation at 10,000g for 10 minutes to remove insoluble material including clay particles and humin. The humic and fulvic acids were separated by acidification of the solution to pH 2.0 by addition of 6M hydrochloric acid. The solution was left to stand for 24 hours, while the humic acid, which is insoluble in acidic solution, precipitated out. The humic acid coagulate was separated from the fulvic acid solution by centrifugation at 10,000g for 10 minutes. The humic and fulvic acids were purified prior to structural investigations. The purification of humics is described in Section 3.5.

Extraction Ratio and Time

The ratio of extractant volume (ml) to substrate weight (g) varies in different studies. The most commonly used ratio is ten volumes of extractant to one weight of soil (Schnitzer et al., 1981; Schnitzer and Schuppli, 1989a; Ciavatta et al., 1990). Other studies have used a higher ratio. Bertha and Choppin (1977) used a ratio of twenty volumes of extractant to one weight of soil. Using a higher ratio of extractant to soil results in the extraction of a greater percentage of the total organic matter present in the soil, but results in a decreased concentration of humic substances in solution. A low extraction ratio reduces the yield of humic substances extracted from the soil, but increases their concentration in solution. Gregor and Powell (1986) used acid pyrophosphate passed through leaching columns of soil with a ratio of three volumes of extractant to one weight of soil. A highly efficient extractant such as sodium hydroxide may be used at lower ratios and still produce a high yield, because the organic matter has a strong tendency to dissolve in it. A limitation of low extraction ratios is that dry soil adsorbs some of the extractant solution which cannot be removed. From these considerations it can be seen that there is a trade off between having:

(i) a concentrated solution of organic matter that represents only a small percentage of the total organic matter in the soil,

(ii) a low concentration of organic matter in the extracted solution that represents a high percentage of the organic matter in the soil.

The contact time of the soil with the extractant is usually 24 hours. A few studies have used 48 hour extractions (e.g. Bertha and Choppin, 1977). Stevenson (1982) suggested using two 12 hour extractions, since this improves the percentage of organic matter extracted. However, additional extraction steps inevitably increase the errors in the scheme and are very time consuming. A single 24 hour extraction is probably the best compromise between ease of use and yield.

Separation of Humic Substances from Suspended Solids

Centrifugation is used in almost all the studies that extract organic matter to separate humic and fulvic acids from suspended solids. A few studies have also employed filtration, for example Nash and Choppin (1980), but this is time consuming and centrifugation is a much more suitable technique. A number of different centrifugation procedures have been used. In a recent study Schnitzer and Schuppli (1989a) used a centrifugation speed of 10000 rpm for 10 minutes, while Bertha and Choppin (1977) used a centrifugation speed of 1000 rpm for 15 minutes, followed by a second centrifugation of 36000 rpm for 30 minutes.

A study by Schnitzer et al. (1981) found that centrifugation speed was critical to the standardisation of results for organic matter extraction. The study looked at the isolation of humic and fulvic acids in a large number of Canadian soils at four different laboratories. Extraction of humic substances was carried out using a mixture of 0.1M sodium pyrophosphate and 0.1M sodium hydroxide. Humic and fulvic acids were separated by acidifying the solution with dilute concentrated hydrochloric acid to precipitate humic acid at pH 2. It was shown that at low centrifugation speeds, the solid residue contained high concentrations of organic carbon, attributable to incomplete separation of the alkaline extractant and solid residue. It is clear that, when the results from different studies are compared, dissimilarities between samples may arise as a function of the variation in centrifugation procedures. Centrifugation speed is essentially a compromise between cost and performance. The authors recommended that centrifugation speed be standardised and suggested that 6000rpm for 30 minutes would be effective.

Sequential Extraction of Humic Substances

The use of a sequential extraction scheme for the extraction of soil organic matter allows the identification of the major humic and nonhumic components of organic matter (Schnitzer, 1991). In a scheme devised by Schnitzer and Schuppli (1989b), the soil sample is leached with a sequence of reagents. Two hot organic solvent extractions are carried out

before two conventional alkaline extractions. The advantage of this scheme is that the waxy esters, long chain alkanes and fatty acids, which may coat humic substances, are removed prior to leaching with alkaline extractants. The procedure allows the scheme to be used on all soils and should increase the yield of humic substances. The soil sample is extracted in a Soxhlet system with n-hexane for 48 hours, which removes alkanes and fatty acids. The soil sample is then leached with chloroform to remove waxy esters and fatty acids. After drying, to remove any traces of the solvent, the soil is leached with 0.1M sodium pyrophosphate followed by 0.1M sodium hydroxide to extract humic substances. The use of two extractions at this stage serves to increase the range of substances extracted and the efficiency of the extraction.

Selectivity of Soil Organic Matter Extractants

The composition of organic matter extracted by particular extractants has been determined and related to the extractant used by several studies (e.g. Schnitzer and Schuppli, 1989a; Piccolo and Mirabella, 1987). Schnitzer and Schuppli (1989a) compared humic substances extracted with 0.1M sodium hydroxide and 0.1M sodium pyrophosphate (pH 9.8). Although sodium pyrophosphate appeared to extract humic substances of higher molecular weight and deeper colour than sodium hydroxide, the differences between them were not significant. Infrared spectra of the humic acids extracted by the two different extractants were very similar, indicating similar chemical characteristics. Nuclear magnetic resonance results indicated that the humic acids extracted by sodium hydroxide were more aliphatic compared to sodium pyrophosphate, which extracted more aromatic humic acids. The differences were found to be highly dependent on soil type. The authors pointed out, that across a range of soil types, the differences between soil types are much greater than between extractants.

Piccolo and Mirabella (1987) reported that sodium hydroxide extracted more of the high molecular weight humic substances than sodium pyrophosphate, apparently in contrast to the results obtained more recently by Schnitzer and Schuppli (1989a). In the Piccolo and Mirabella (1987) study, the concentration of sodium hydroxide used was 0.5M, compared to 0.1M in the Schnitzer and Schuppli (1989a) study and the sodium pyrophosphate was pH adjusted with phosphoric acid to neutrality. These differences invalidate any comparison between the studies. In addition the Piccolo and Mirabella study (1987) investigated humic substances extracted from peat, so the results might be expected to differ from studies of soils because of the different substrate. In a comparison of the yields obtained by using these extractants, Piccolo and Mirabella (1987) found that sodium hydroxide extracts twice the

amount of organic matter from peat as sodium pyrophosphate at pH 7.0. The sodium hydroxide tends to remove free organic matter, whereas sodium pyrophosphate, with its greater complexing power, extracts organic matter associated with clay minerals or iron oxides. Carter et al. (1992) studied humic acids extracted from sediments by a range of extractants. The complexation capacity of humic acids was a function of the alkaline strength of the extractant, emphasising the need for care in the analysis of these results.

Acid Pretreatments

The aims of acid pretreatments are to reduce the chemical alteration of soil organic matter during the extraction and to reduce the ash content of the extracted humics. After acid pretreatment, Goh and Reid (1975) found that both the yield and polydispersion of humic substances extracted had been greatly improved and was accompanied by a decrease in the ash content of the humic substances. An acid pretreatment using 0.3M hydrofluoric acid was used by Gascho and Stevenson (1968) to remove hydrated silicate minerals, prior to the recovery of organics by 0.03M sodium hydroxide and 0.02M sodium pyrophosphate. In a study of acid pretreatments of soil organic matter Goh and Reid (1975) observed that prolonged exposure of soils to dilute acid resulted in:

(i) acid induced polymerisation,

(ii) losses of extractable carbon,

(iii) adverse chemical modifications of humic substances.

To avoid these problems they concluded that the contact time of the acid pretreatment should be kept to a minimum, preferably less than 3 hours. Alternatively, the acid treatment may be used after the soil organic matter extraction, as a purification step, to reduce the ash content (Gascho and Stevenson, 1968). Schnitzer (1982) recommended that soils be treated with dilute acid, for example 0.05M hydrochloric acid, to remove free carbonates prior to carrying out a sodium hydroxide extraction. Keefer et al. (1984), in a study of metal-organic components, used a treatment with 0.1M hydrochloric acid for 7 days designed to remove loosely bound metals, but to leave organo-metal complexes intact. A 1M hydrochloric acid treatment for 24 or 48 hours was used by Nash and Choppin (1980), however, this was to remove iron prior to sodium hydroxide extraction of soil organic matter. Acid pretreatments are particularly useful when the humic substances are to be analysed for their structure. In the present study it was felt that the use of an acid pretreatment increased the chance of removal of the metal from the organic matter, so acid pretreatments were not used.

Oxidation of Humic Substances

The treatment of soils with alkaline extractants to remove organic matter has been criticised because it could result in oxidation or hydrolysis of humic substances (Stevenson, 1982). In a study of alkaline extraction of organic matter from soil Bremner (1950) found that oxygen was adsorbed and carbon dioxide was released, which indicated that oxidation of organic matter had taken place. The problem was subsequently solved, or at least very much reduced, by carrying out organic matter extractions under a nitrogen atmosphere (Schnitzer and Skinner, 1968). Swift and Posner (1972) looked at the problem from a different perspective by considering oxidation of humic substances in the natural environment. They concluded that the variation found in natural humic substances was a function of the oxidation state. Mendonca et al. (1991) found that in tropical soils the susceptibility of humic substances to oxidation was generally low, depending on the soil structure and cultivation.

Oxygen adsorption during the extraction of soil organic matter is dependent on the pH and type of extractant used. An extractant solution of 0.1M sodium hydroxide was found to be at pH 12 after a 24 hours extraction, compared to pH 9-9.4 for an unadjusted 0.1M sodium pyrophosphate extraction (Schnitzer and Schuppli 1989a). Bremner (1950) observed that 700-900mm^3 oxygen per 0.2 grams of soil was adsorbed by 0.1M sodium hydroxide, whilst unadjusted sodium pyrophosphate solution adsorbed only 4 to 6% of that amount. The volume of oxygen adsorbed by sodium pyrophosphate adjusted to pH 7.0 was even lower, but extraction efficiency was greatly reduced.

3.4.3 Organic Matter Extraction Using Organic Solvents

Reducing Chemical Modifications to Humic Substances During Extraction

Organic solvents were proposed for the extraction of humic substances from soils in an attempt to overcome the artefacts induced in humic substances by the use of harsh alkaline chemical extractants. These solvents extract humic substances with lower amounts of silicate impurities than inorganic extractants (Hayes, 1991). Humic substances obtained from inorganic extracts require purification prior to structural investigation. Piccolo and Mirabella (1987) compared organics extracted by two inorganic (0.5M sodium hydroxide, and 0.1M sodium pyrophosphate pH 7) and three organic extractants (dimethylsulphoxide, N,N dimethylformamide, and acetone). They observed that organic extracts contained increased amounts of lower molecular weight fractions, compared to inorganic extractants. The humic substances extracted by organic solvents were less humified and contained lower amounts of

highly condensed polymers than those extracted by sodium hydroxide or sodium pyrophosphate. There are two main disadvantages of using organic solvents for organic matter extraction:

(i) Contamination by nitrogen and sulphur from the solvents is difficult to remove (Schnitzer and Schuppli, 1989b),

(ii) Efficiency of the extraction is about 10% of that of sodium hydroxide. (Piccolo and Mirabella, 1987).

Organic extractants are useful when studies of the structure of organic matter are being carried out and small quantities of humic substances are sufficient for the analysis. When a high yield is required, it is clear that inorganic extractants are superior.

Chemistry of Organic Extractants of Soil Organic Matter

The properties of good organic solvents have been outlined by Hayes (1985; 1991). The solvent should have a high electrostatic factor, the product of dipole moment and relative permittivity. A high base parameter pk_{HB} is desirable, this is defined as the relative strength of the acceptor when an H-bonded complex forms with a suitable OH reference acid, such as ethanol (Taft et al., 1969). Examples of extractants that fulfil these criteria are dipolar aprotic solvents such as acetone, dimethylformamide, and dimethylsulphoxide. These extractants are used in a mixture with water and hydrochloric acid at pH 1.8. Strong association of these solvents with water molecules enhances the hydrogen bonding capacity of the mixture (Piccolo and Mirabella, 1987). The acid serves to break the polyvalent salt bridges between organic molecules and mineral compounds.

Dimethylsulphoxide (DMSO) fulfils the criteria for good organic solvents. Anions are sparing soluble in DMSO, whilst cations readily dissolve in it. The solvent can associate with the phenolic and carboxylate functional groups that occur in the humic molecule. The solvent breaks inter- and intra- strand hydrogen bonds allowing dissolution of the humic macromolecules. The non-polar backbone of the molecule, allows it to associate with non-polar groups occurring in the humic macromolecule, enhancing dissolution of humic substances. DMSO associates strongly with water. The association with water inhibits the interaction of the S=O site on DMSO with the acidic groups on the humic macromolecules and slows the dissolution of dry humic substances in DMSO (Hayes, 1991).

Hayes (1991) found that DMSO removed substantial amounts of organic matter after extraction with sodium hydroxide and sodium pyrophosphate. The residue of humic

substances, insoluble in sodium pyrophosphate and sodium hydroxide, is classified as humin. Hayes (1991), analysed this material and found that it had properties resembling fulvic acid. It was hypothesised that the humic material was fulvic acid, either with the acid groups oriented towards the clay surface, or with a protective wax layer covering the acid groups. This hypothesis would explain the solubility of these humics in organic solvents and their insolubility in inorganic extractants.

Organic Matter Extraction Using Distilled Water at High Temperature

A new method of soil organic matter extraction, using distilled water at high temperatures (150°C, 200°C, 250°C) and pressure (17.2MPa), has been developed by Schnitzer et al. (1991). The method was tested on four soils and recoveries of nitrogen and carbon were found to be better than for the 0.1M sodium pyrophosphate method. The composition of the humic material extracted was found to be dependent on the temperature of the extraction. Thermal degradation of humic substances occurs at temperatures in excess of 250°C (Schnitzer et al., 1991). The major drawback of this procedure is the need for specialist equipment to reach the high temperatures and pressures required.

Organic Solvent Extraction of Soil Organic Matter, Conclusions

From these studies it can be concluded that when yield is not an important consideration, organic extractants are good for structural studies of organic matter. Organic extractions lead to fewer structural artefacts than inorganic extractions. In the study of metal binding to humic substances a high yield is important, as the metal concentrations in humic substances can be very low. Large quantities of humic material are required to obtain accurate heavy metal concentrations. For this reason the present study uses inorganic extractants to study metals associated with humic substances. The scheme uses mild reagents to attempt to reduce the possibility of displacement of the metals from the organic matter.

3.5 Purification of Humic Substances

The main objectives in the purification of humic substances are:

(i) Minimisation of the ash content and

(ii) Removal of the nonhumic molecular components of organic matter

Purification of humic substances is essential before structural investigation can be made. Humic acids may be purified by washing with distilled water, washing with acid, or repeated extraction and fractionation procedure.

3.5.1 Humic Acid Purification

In a study of humic substances extracted by a range of inorganic and organic extractants, Piccolo and Mirabella (1987) purified humic acids by dialysis against distilled water, prior to drying and structural analysis. Other studies have used repeated dissolution and precipitation of humic acids to remove impurities (e.g. Nash and Choppin, 1980).

The purification of humic acids by acid treatments has been used by Schnitzer and Schuppli (1989a,b) and Schnitzer (1982). In these studies the humic acid was dissolved in 0.1M potassium hydroxide under a nitrogen atmosphere. Potassium chloride was added to the solution until the system had a potassium concentration that was 0.3M. The solution was left to stand for 4 hours before centrifugation, to remove suspended solids, at 10000g for 10 minutes. The humic acid was then precipitated by acidifying the solution to pH 1. The humic acid was allowed to coagulate and was removed by centrifugation at 10000g for 10 minutes. The procedure was followed by two acid treatments to reduce further the ash content. The acid solution used for the acid treatments consisted of 5ml of concentrated hydrochloric acid and 5ml of 52% hydrofluoric acid, diluted to 1000ml with distilled water. The humic acid precipitate was shaken with 300ml of the acid mixture for 24 hours. The suspension was centrifuged for 10 minutes at 10000g. The acid treatment was then repeated and the purified humic acid was washed in distilled water and dried in a desiccator ready for analysis.

3.5.2 Purification of Fulvic Acids

History and Development of the Use of Amberlite XAD Resins

The development of XAD macroporous resins in the 1970s allowed humic substances to be isolated and concentrated from natural waters much more effectively than previous methods. Previously, methods designed to separate organic compounds from natural waters had made use of inorganic adsorbents such as activated carbon, alumina, silica gel, magnesia and calcium carbonate (Mantoura and Riley, 1975). Many authors reported that the recovery of humic substances from these adsorbents was poor. There were two reasons for this:

(i) adsorption of humic compounds on these adsorbents was inefficient,

(ii) humic material became strongly bound to the adsorbent making elution difficult.

Methods for the concentration of organic matter included vacuum distillation, freeze drying and ultrafiltration. These methods are rather time consuming and difficult to carry out

due to the very low concentrations of humic matter in the majority of natural water samples. Before the advent of XAD macroporous resins other organic adsorbents had been tried. Mantoura and Riley (1975) experimented with nylon and microporous polystyrene beads (Amberlite XAD-1 or XAD-2). However, their desorption capacities were low and the recoveries of humic acid were poor.

The use of XAD resins has allowed the humic substances present in natural waters to be concentrated thousands of times, to yield quantities and concentrations suitable for analysis (Aiken, 1985). These techniques have also been applied to the purification of humic substances, in particular fulvic acids, extracted from soils and sediments. In soils, the problem associated with the isolation of humic substances is not so much one of concentration, but the problem of isolating specific groups of substances from the soil free of contamination by other fractions containing metals. The use of XAD resins has largely overcome the difficulties associated with previous methods used for the concentration and purification of fulvic acids from natural waters, soils and sediments. The purification of fulvic acids aims to remove:

(i) inorganic salts,

(ii) low molecular weight organics

(iii) nonhumic organics.

The advantages of using XAD resins over other adsorbents are their high adsorption capacity and ease of elution (Aiken, 1985). A number of different XAD resins have been used to purify humic substances. The section that follows describes the properties of the various XAD resins and reviews their use in the purification of fulvic acids. These resins have been used in a number of studies of fulvic acids (e.g. Keefer et al., 1984) where XAD-8 resin was used to purify fulvic acids for a study of metal binding to organic matter.

Chemical and Physical Properties of Amberlite XAD Resins

XAD resins are essentially non-ionic macroporous copolymers with a large surface area. They can be divided into two groups, based on their chemical composition:

(i) *Styrene divinylbenzene copolymers* have aromatic units in their structure. They are difficult to wet, adsorb very little water and have no ion-exchange capacity. The resins XAD-1, XAD-2, and XAD-4, are examples of this type of resin.

(ii) *Acrylic ester polymers* are aliphatic and have no aromatic units. These resins are of intermediate polarity, they are hydrophilic and have a very low ion exchange capacity. XAD-7 and XAD-8, both poly(methylacrylate) resins, are examples of this type of resin.

XAD Resin Properties

The distribution coefficient of fulvic acid on XAD is defined as:

K_D= mg material adsorbed by resin per gram of resin
mg material in solution per millilitre of solution from Aiken et al. (1979)

The distribution coefficient is a measure of the efficiency of the resin at trapping fulvic acids. It follows that a high distribution coefficient of the fulvic acid on the resin is a desirable property of the resin. Aiken et al. (1979) investigated the distribution coefficients of fulvic acid on XAD-8 over a range of pH from pH 1 to pH 7. The study found that the distribution coefficient of fulvic acid on XAD-8 was highest at low pH and declined rapidly as pH was increased. The optimum pH for adsorption of fulvic acid on XAD-8 resin was pH 2. More acidic solutions may cause denaturization of the fulvic acid molecules. Distribution coefficients for XAD-7 and XAD-8 are higher than for XAD-1, XAD-2 and XAD-4.

Fulvic Acid Adsorption to XAD Resins

Adsorption of fulvic acids onto the styrene divinylbenzene copolymers XAD-1, XAD-2 and XAD-4 is slow due to unfavourable kinetics (Aiken, 1985). Elution of fulvic acids from XAD-1, XAD-2 and XAD-4 is difficult, which suggests that the low elution efficiency of fulvic acids from styrene divinylbenzene resins is due to charge-transfer complexation, between the resin and the fulvic acid. This type of complexation can occur when an aromatic molecule has π–electron pairs in its orbitals that it donates to another organic compound, in this case fulvic acid. The acceptor molecule must be one of the following types of molecule: (i) polynitro compounds, (ii) phenols and (iii) quinones. It is known that fulvic acids may contain phenolic and quinone groups (Schnitzer and Khan, 1972).

Fulvic acids are applied to columns of acrylic ester resin, XAD-7 or XAD-8, in acidic solution. Hydrogen ion exchanged (protonated) fulvic acids bind to XAD-7 and XAD-8 resins at low pH and are trapped on the column. Salts, small molecules and nonhumic macromolecular organic compounds, such as polysaccharides, may then be removed by washing. Fulvic acids are released from the resin by raising the pH causing the acidic groups to ionise and the fulvic acid molecules desorb from the resin. Unlike styrene divinylbenzene copolymers acrylic ester resins XAD-7 and XAD-8 are aliphatic and cannot undergo charge-transfer complexation. Elution of fulvic acids from these resins has been found to be 98% efficient (Aiken et al., 1979).

Pore Size

Pore size and specific surface area are important properties controlling the performance of XAD resins. An important consideration in choosing a suitable resin for the purification of fulvic acid is the pore size relative to the size of the fulvic acid molecule. Estimates of the sizes of fulvic acid molecules show that they are rod like molecules with a width of about 71 nm and a length of 400 nm (Chen and Schnitzer 1976). To accommodate a molecule of this size, avoiding steric hindrance effects, requires a pore size that is greater than 1000nm. Table 3.1 lists properties of the different types of XAD resins in their dry state. It is important to remember that both XAD-7 and XAD-8 swell up when they adsorb water which will alter these properties, in particular the pore size will increase. From Table 3.1 it can be seen that XAD-4 has a smaller pore size than that estimated to be necessary for fulvic acid molecules to be adsorbed, therefore the exclusion of fulvic acids from XAD-4 is likely to occur. Aiken et al. (1979) observed this effect, in a comparative study of the different types of XAD resin. The capacity of XAD-4 was found to drop sharply as the molecular weight of fulvic acid increased from 2000 to 5000. This is in marked contrast to XAD-8 where the distribution coefficients of molecules of molecular weight 5000 were found to be slightly higher than those of molecules of molecular weight 2000, a direct result of size exclusion on XAD-4 (Aiken et al. 1979).

Table 3.1: Properties of XAD-8 Resins

from Aiken et al. (1979)

Resin	*Composition*	*Av. pore diameter*	*Specific surface*
		nm	area m2/g
XAD-1	Styrene divinylbenzene	200	100
XAD-2	Styrene divinylbenzene	90	330
XAD-4	Styrene divinylbenzene	50	750
XAD-7	acrylic ester	80	450
XAD-8	acrylic ester	250	140

From these properties it can be seen that acrylic ester resins, XAD-7 and XAD-8, are the most suitable resins to use for the purification of fulvic acids from inorganic extracts. The advantages of acrylic ester polymer resins over styrene divinylbenzene resins are as follows:

(i) Their adsorption capacity is higher,

(ii) Adsorption of fulvic acids onto the resins is more rapid,

(iii) Equilibrium is achieved more quickly,

(iv) Elution is more efficient.

Elution of Fulvic Acids

In a study by Aiken et al. (1979) elution of fulvic acid with 0.1M sodium hydroxide was found to be highly effective. Elution from XAD-8 was found to be more rapid than from XAD-7. The rapid elution of XAD-8 with 0.1M sodium hydroxide avoided the bleed problems that sometimes occur with these resins. XAD-8 was shown to cause less resin bleed problems than XAD-7. The study showed that methanol was an inefficient eluant due to its limited ability to dissolve humic substances. In contrast Gregor and Powell (1986) recommended elution of fulvic acid from XAD-7 columns with distilled water at pH 6.5. They claimed that 98% of the fulvic acid adsorbed on the column was eluted at this pH. Avoiding the high pH of the 0.1M sodium hydroxide elution was considered desirable, as the rapid change in pH from pH 2 to pH 13 is a potential cause of structural alteration of the fulvic acid. The authors claim that the high pH found necessary by other authors was because inadequate filtration of the sample led to blocking of the resin pores.

Preparation of the Sample

Organic matter occurs in two main forms in both soils and natural waters: dissolved and particulate. The distinction between them has been arbitrarily defined as the separation achieved by a 0.45μm filtration. Organic matter that passes through the filter is classified as soluble and the organic matter trapped by the filter is classed as particulate (Aiken, 1985). Soluble humic substances have been defined as substances that on passing through a 0.45μm filter have a column distribution coefficient of greater than 50 on an XAD-8 column at pH 2 (Malcolm, 1985). Particles greater in size than 0.45μm have been found to block the pores of the XAD resin (Aiken, 1985). Filtration of the soil extract or natural water sample is, therefore, essential for the resin to function correctly. Ideally, the samples should be passed through a 0.1μm filter, but this leads to a considerably longer processing time (Aiken, 1985). The 0.025μm filtration used by Gregor and Powell (1986) explains their ability to use a pH adjustment to pH 6.5 to elute fulvic acids without the need for 0.1M sodium hydroxide.

Lobartini et al. (1989) found that blackwater samples, where high concentrations of humic substances make the water appear black, contained humic matter present as a metal-humic chelate. They suggested that the acidification of the blackwater sample, prior to its treatment on the XAD-8 column, lead to a release of the metal, which would leave the

carboxylic acid groups free to react with methyl groups of aliphatic substances. The authors do not mention which metal or metals are likely to be present. The stability constants of the metal humic chelate depends on the metal element present and the pH of the solution. Hydrogen and metal ions compete for the anionic binding sites of fulvic acid, conversely hydroxide and fulvic ions compete for cationic metal ions. The physical parameters pH, ionic strength and temperature determine the complexes formed and their stabilities. Increasing pH leads to increased fulvic acid availability and decreased metal availability. As pH increases the stability constants increase and then decrease after a certain point (Malcolm 1985). Metals with larger stability constants such as lead, copper, aluminium and iron are unlikely to be released. Metals with lower stability constants such as zinc, nickel, chromium, cobalt or manganese stand an increased chance of being released. The most likely metals to be released are those with low stability constants including: calcium, magnesium and cadmium. At low pH the metal fulvic acid complexes are in true solution. At higher pH values the complexes may exist in true solution or may be in colloidal form.

Organic Matter Extraction from Soils

The majority of studies that use inorganic extraction of organic matter from soils have investigated the structure of organic components. Inorganic extractants are the most suitable for quantitative studies, as the yield of humic substances obtained by the use of these extractants are much higher than those obtained using organic solvents.

3.6 Iron and Manganese Oxides

Iron and manganese oxides are an important sink for heavy metals in soils and sediments. Heavy metals may be adsorbed to the oxide surface or, in the case of crystalline oxides, bound in the crystal structure.

A variety of different extractants have been used to extract iron oxides from soils and sediments. Table 3.2 lists the extractant used by various researchers for the extraction of the various different forms of iron and manganese oxides found in soils.

A number of studies have investigated the effect of the removal of iron oxides on the adsorption of heavy metal elements. The effect of removing hydrous iron oxides from two acidic soils, pH 4.5 and pH 4.7, on the adsorption of cadmium, copper, zinc and lead was

studied by Elliot et al. (1986a). The iron oxides were removed from the two ferruginous subsoils, a silty clay loam and a sandy clay soil, by the use of a dithionite citrate bicarbonate extractant solution. The results of heavy metal batch adsorption experiments showed that the removal of iron oxides actually resulted in an increase in heavy metal adsorption. In another study using dithionite-citrate-bicarbonate to remove iron oxides, Gharbru et al. (1990) reported similar results. Cation exchange capacity was found to increase after the removal of iron oxides.

Table 3.2: Extractants Used to Determine the Forms of Iron Oxides in Soils

Extractant	*Form of Iron Extracted*	*Reference*
Dithionite-Citrate-Bicarbonate	Crystalline Iron Oxides	Elliott et al. (1986a,b)
0.1M Hydrochloric acid	Amorphous Iron Oxides	Singh & Gilkes (1992)
Hydroxylamine hyrochloride	Amorphous Iron Oxides	Chao (1972)
5M Sodium hydroxide concentration step followed by 1M HCl dissolution	Goethite and Hematite	Singh & Gilkes (1992)
Potassium pyrophosphate at pH 7	Amorphous Iron Oxides	Bascomb (1968)

In contrast to these studies a study by Cavallaro and McBride (1984) showed that zinc sorption was reduced as a result of iron oxide removal by dithionite citrate bicarbonate. They suggested that at low pH (4 - 6 for copper and 5 - 7 for zinc) the reactive surfaces of crystalline, microcrystalline and non-crystalline iron oxides were an important sink, resulting in the immobilisation of zinc and copper, particularly in subsurface soil horizons. Removal of organic matter did not cause a decrease in zinc and copper sorption. A study of the associations of minor elements, including heavy metals, was conducted by Singh and Gilkes (1992). Iron oxides were found to contain a large proportion of the cobalt, chromium, copper, manganese, nickel and zinc in the soils studied. The results of the study, of some 39 soils from south-western Australia, indicated that the metals were present inside the structure of the iron oxides as well as adsorbed to the surface.

Mechanisms Controlling the Behaviour of Iron Oxide - Heavy Metal Associations In Soils

The different results obtained by the various studies of the removal of iron oxides from soils suggest that more than one mechanism may be acting to control the associations of heavy metals with iron oxides. The increase in cation exchange capacity after the extraction of iron oxides using dithionite-citrate-bicarbonate, observed in the Gharbru et al. (1990) study, was attributed to the removal of iron oxide coatings that prevent cation binding to cation exchange

sites. The silicate layer, largely responsible for cation exchange complexation, has a net negative charge and therefore attracts cations. A hydroxy polymeric iron oxide coating on silicates would have a net positive charge, preventing the exchange of cations at the surface (Elliot et al., 1986b). When field soils have a low zero point of charge, they carry a negative charge at the soil pH resulting in the attraction of cations to the negative charge on the soil surface. The positive surface charge on the hydroxy polymeric iron oxide coating was a result of the high pH of the zero point of charge of the surface coating. Removal of iron oxides results in a reduction in the zero point of charge and corresponding increase in the attraction of the surfaces for cations.

Batch adsorption experiments using solutions spiked with ferric ions were carried out by Elliot et al. (1986b). The results of these experiments suggested an alternative mechanism. They showed that ferric ions suppressed adsorption of heavy metals due to adsorption of iron cations to cation exchange sites. The removal of iron cations from exchange sites by the dithionite-citrate-bicarbonate buffer resulted in an increase in cation exchange capacity that more than offset the loss of adsorption capacity from the removal of the iron oxide substrates. The implication was that the iron ions were blocking the cation exchange sites, explaining the increase in cation exchange capacity after the removal of iron oxides.

Humic and Fulvic Acid Interactions with Iron and Manganese Oxides

Humic substances form strong association with iron and manganese hydrous oxides. The humic substances are mainly bound by simultaneous reaction with two functional groups, such as simultaneous phenolic and carboxylic acid binding, with only minor binding attributed to carboxylic acid functional groups alone (Schnitzer, 1969). A model system of synthetic iron (III) hydrous oxide and synthetic humic macromolecules was studied by Bartoli et al. (1992). Adsorption was determined at pH 6, similar to the pH found in many soils and freshwater systems. The study showed that the mechanism of adsorption of the humic molecules onto hydrous iron oxides was by surface charge neutralisation. The net negative charge on humic molecules neutralised the positive charge on the hydrous iron oxides. The evidence offered to support this hypothesis was the observed reduction in the zero point of charge from pH 7.3 to pH 5.6.

Although in general iron oxides are a very important sink for heavy metals, there are occasions when the removal of iron oxides may result in an increase in the capacity of the soil to bind heavy metals.

4 Sample Collection And Experimental Methods

4.1 Criteria For Sampling Sites

The soil profiles and heavy metal inputs at each of the four sites chosen for the present study are described in this chapter. The techniques used to determine the soil properties pH, cation exchange complexation, organic matter content and iron oxide composition and the general laboratory procedures are outlined in Section 4.2. The methods for the sequential extraction of heavy metals and the fractionation of organic matter into its humic and fulvic acid components are given in detail at the end of the chapter.

The heavy metal inputs were aerial inputs from metal smelters. The criteria for the choice of heavy metal input are discussed in Section 1.1. One type of aerial metal input that was considered was metal released from the burning of fossil fuels in coal fired power stations. Close inspection of previous studies that have investigated emissions of trace metal elements from power stations showed that considerable quantities of heavy metals were released from the burning of fossil fuels (Lim, 1978; Cannon and Swanson, 1980). However, the high chimneys used in modern power stations release heavy metals over a large area, resulting in low heavy metal concentrations in the surrounding soils that are difficult to distinguish from the background levels. Emissions of heavy metals from the shorter chimneys of metal smelters are more localised, resulting in high concentrations of metals in the area around the smelter.

The main consideration in the selection of field sites was to find soils with sufficiently high levels of heavy metal contamination to allow the metal analysis to be carried out by flame atomic absorption spectrophotometry, facilitating the rapid analysis of the large number of samples that are needed for a study of this type. Flame atomic absorption spectrophotometry is far less time consuming than the graphite furnace techniques needed for the detection of very low metal concentrations. High heavy metal concentrations are also of greater concern in an environmental context. The heavy metal concentrations in extracts from the sequential extraction scheme are inevitably considerably lower than the total metal concentrations in the soil. To overcome these problems, only soils with a relatively high degree of heavy metal contamination were chosen for this study. An added complication in the selection of sites was the desire to have soils of widely differing pH. It was considered highly advantageous to study several different soil types receiving heavy metals from the same source, so that the variation between samples could be attributed to differences in soil properties rather than differences in metal inputs. However, it was very difficult to find sites that fulfil both these criteria.

4.1.1 Choice of Sites

Field sites were chosen in areas that were known, or expected, to have high concentrations of the heavy metals of interest. A number of sites were considered for the studies including: nickel in serpentine derived soils on the Lizard peninsular, sites around disused nineteenth century lead smelters in the Swaledale and Wensleydale area of the north Pennines and similar sites in the Mendips and North Wales. Out of the potential situations two sites were chosen, Hallen near Avonmouth and Ringinglow near Sheffield, both these sites had received metal from smelting activity and are described in detail below. Pilot studies of soils from the Ringinglow area were performed to check their suitability for the study, by determination of their pH and total metal concentrations. The results indicated three soil profiles were suitable for the study. The total digestion results for an undisturbed soil profile with an aerial metal input were expected to show a decline in the total metal concentration with depth in the soil profile, which was the case at all the sites studied.

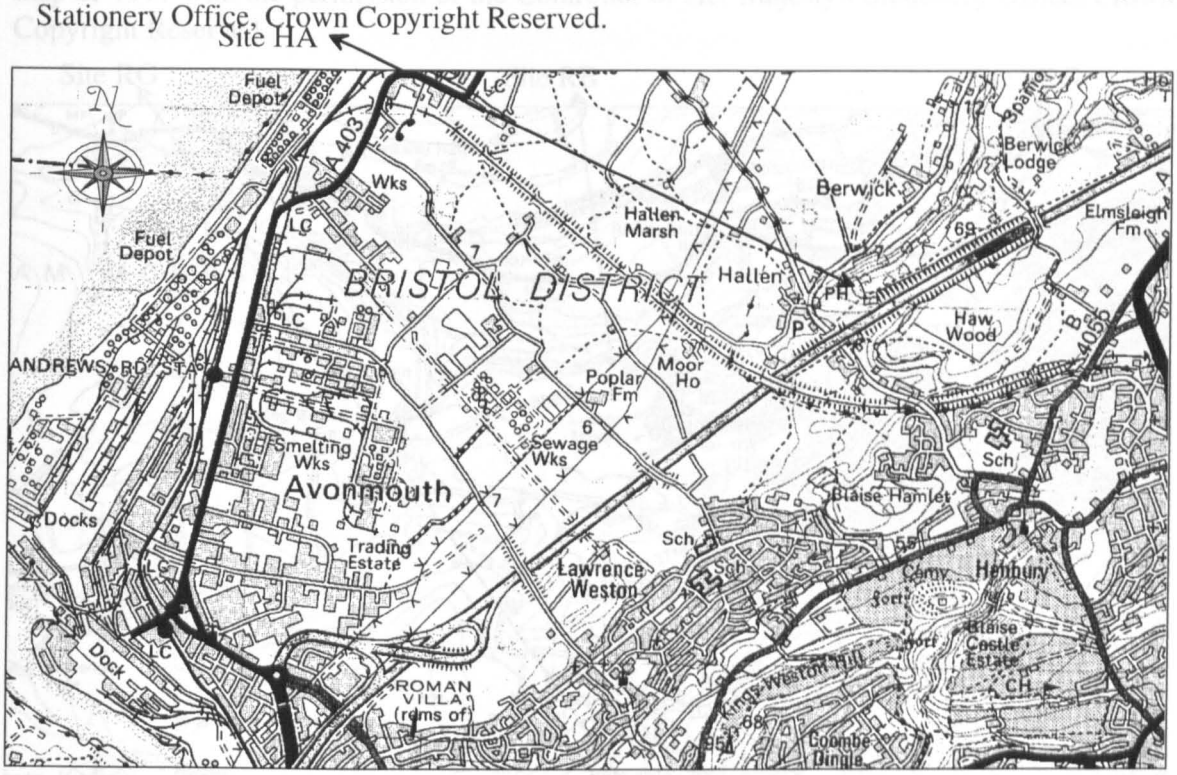
Hallen Wood, Berwick Ridge, near Avonmouth.

In the early stages of the study the techniques were developed on soils from Hallen wood (OS grid reference ST 555 802), an old oak-hazel wood (*Quercus robur, Corylus avellana*). The site receives heavy metal inputs from the industrial complex and smelting works at Avonmouth, on the east bank of the Severn Estuary (Figure 4.1). The use of these samples allowed the methods to be developed on soils where the very high concentrations of lead, zinc, copper and cadmium made the metal determinations comparatively easy. Lead and zinc smelting has been carried out on this sites since 1929 and continues to this day. The lead-zinc smelter has been owned by MIM holdings since 1993 and its annual production is currently 120,000 tonnes of zinc and 55,000 tonnes of lead. There are additional inputs of metals from a municipal incineration plant and the M5 motorway which is 300m to the east of the site. The total concentrations of lead and zinc in the top soil profiles were approximately 1-3mg/g.

Ringinglow Southwest Sheffield

Subsequent studies examined three soil profiles from the Ringinglow area near Sheffield (Figure 4.2). These were: a neutral stagnogley, site RG (OS SK 285 835); an acidic podzol, site RB (OS SK 280 863) and an acidic brown earth, site SRG (SK 298 838). The main input of lead at the sites was from mining and smelting activity. Anthropogenic inputs of nickel and zinc from industrial activity in the Sheffield region as well as from mining and

Figure 4.1 Map of Site at Hallen, site HA, a brown earth. Reproduced from the Ordnance Survey's 1:50,000 scale map of 1990 with the permission of the Controller of Her Majesty's Stationery Office, Crown Copyright Reserved.



smelting are also important (Markert and Thornton, 1990). The soil profiles investigated were in the vicinity of a disused nineteenth century lead smelter.

The soil profiles at Ringinglow were chosen because the chemical forms, although not the concentrations, of the heavy metal inputs were similar for all three soil profiles. However, the soil profiles were very different in terms of soil type, organic matter content and distribution, and pH allowing the comparison of heavy metal speciation in different soil profiles with the same metal input. The heavy metal concentrations found at this site were perhaps more representative of those found in the majority of contaminated soils.

Table 4.1 Summary of Field Sites

Full details of soil profile descriptions are given in Appendix 1.

Site	*Elevation (m)*	*Vegetation*	*Soil Type*
Site HA, Hallen wood	60	Deciduous woodland	Brown Earth
Site RG, Ringinglow	350	Grassland	Cambic Stagnohumic Gley soil
Site RB, Ringinglow	290	Heather	Ironpan Stagnohumic Podzol
Site SRG, Ringinglow	300	Deciduous woodland	Typical Brown Earth

Figure 4.2 Map of Sites at Ringinglow Site RG, a neutral stagnogley; site RB, an acid podzol; and site SRG, an acidic brown earth. Reproduced from the Ordnance Survey's 1:50,000 scale map of 1977 with the permission of the Controller of Her Majesty's Stationery Office, Crown Copyright Reserved.

4.1.2 Sample Collection

The sampling scheme was designed to collect material from different depths in the soil profile. To carry out a study of metal distributions down a soil profile, it is important to choose soils that have not been disturbed from the time of the heavy metal input, which effectively rules out all soils that have been in cultivation. Soil under a woodland canopy may be used, but it is important to recognise that some cycling of metals through the vegetation is likely to have taken place. Deposition of metals under a canopy may show significant spatial

variability due to canopy soil interactions. However, over long periods of time, changes in the canopy structure will probably result in a reduction of this type of variation. The most suitable soils for down profile studies are those under grassland or scrub vegetation, although woodland soils are less likely to have suffered disturbance.

The first application of the sequential extraction scheme at the Hallen site was carried out at four depths in the soil profile down to 20cm. The results of this pilot study showed that sampling to this depth was insufficient to give a good depiction of metal distributions down the soil profile. To represent the biologically active part of the soil profile, samples were collected at six depths: 0-5cm, 5-10cm, 10-15cm, 15-25cm, 25-35cm and 35-50cm. The increments are narrowest in the top layers where metal concentrations decrease most rapidly.

Samples were extracted using a 2.5cm bore stainless steel soil auger that was washed with distilled water after each sample was taken to avoid contamination. Four sites, each having a different soil type, were sampled (Table 5.1). The equivalent of a single soil core was collected for each soil type. The samples of each depth in the soil profiles were collected by combining soil material at the same depth from 16 soil cores removed from a regularly spaced array within a 2 meter x 2 meter area. No attempt was made in these studies to look at spatial variation across the field sites, as this is considered to be a major problem in its own right. Instead, the studies concentrated on the distribution of metals down the soil profile and between various fractions in the soil. Given the diffuse nature of aerial inputs of metals to soils, the spatial variability of total metal concentrations over this area could be expected to be small. However, spatial variability may become important when canopy effects, as described above, are significant, or where soil profile conditions are spatially variable.

Sample Preparation

All soil samples were air dried at 105°C for 48 hours immediately after collection. The dried soil was ground with a pestle and mortar to pass through 2mm and 500μm meshes. Material that would not pass through the 500μm mesh was discarded. Litter samples were ground in an electric grinder and sieved through a 500μm mesh.

4.2 Physiochemical Property Determinations

Replication

All measurements and determinations were made on six replicates. The soil samples were mixed thoroughly during grinding and before subsamples were taken at random for analysis. Methods for the determination of iron compounds are included in Section 4.4.1.

Errors and Accuracy

Samples and chemicals were weighed out on four figure balances. Volumes were measured by pipette and cross checked by weighing on a four figure balance. All standards were made up accurately in A-grade glassware. Extracting solutions were made up in A-grade glassware where possible. The errors in weight and volume were less than 0.2% in all cases. These errors were found to be insignificant compared to other sources of error and variation.

Measurement of pH

The pH was measured by the glass electrode-calomel electrode pH meter method of McLean (1982). The soil was made into a slurry by thoroughly mixing equal volumes of distilled water and freshly collected soil in a small beaker with a glass rod. It was then allowed to settle for ten minutes before the pH was measured with a pH electrode. Six replicate measurements of the pH of each soil sample were made.

Cation Exchange Complexation

This soil property was measured by the Soil Survey Laboratory Method, based on Bascomb (1964). The magnesium concentrations were determined by atomic absorption spectrophotometry instead of by titration.

Loss on Ignition

Approximately one gram of soil was measured into each crucible. Six replicates of each soil sample were determined. The samples were placed in an oven at 105°C for 6 hours to dry and then stored in a desiccator prior to weighing at ambient temperature. This procedure was repeated after the ignition stage to make sure that the weighings were carried out under identical conditions. The samples were placed in a thermostatically controlled furnace and were heated to 375°C for 18 hours. The samples were allowed to cool and were removed from the furnace. The samples were then treated as described above, prior to weighing. The loss on ignition was calculated by expressing the weight loss as a percentage of the dry soil weight.

Organic Matter Determination

The concentrations of organic matter in soils were estimated by the method of Walkley and Black (1934), modified by Baker (1976).

Acid Digestion for Total Metal Concentrations

Total digestions were carried out in 100ml conical flasks on a heated sand bed. 0.5 or 1.0 grams of soil were weighed into the conical flasks. The samples were refluxed with excess concentrated nitric acid for 4 hours. After the digests had cooled down, the supernatants and

residues were washed into a 25ml volumetric flask through a Whatman No. 42 filter paper. The solutions were diluted to volume and decanted into 25ml vials. Heavy metal concentrations were determined by atomic absorption spectrophotometry.

4.2.1 Atomic Absorption Spectrophotometry

The metal concentrations were determined by flame atomic absorption spectrophotometry, with deuterium lamp background correction, using a Philips Pye Unicam SP9 atomic absorption spectrophotometer. Total digestions of soil samples were determined for lead, zinc, copper, cadmium, nickel, iron and manganese. Metals that were undetectable in the total digest of a soil sample were not determined in other extractions. The metal sensitivities are reported in Appendix 2.

Standards

Metal standards were made in solutions containing the reagents used for the extraction. Double distilled water was used in the preparation of all standard solutions. The standard ranges were chosen to allow a wide variation in the metal concentration that could be determined. Avoiding unnecessary dilutions is highly desirable, as the preparation of large numbers of dilutions is likely to lead to errors. If metal concentrations, were too high for an accurate reading to be obtained, a less sensitive wavelength was used. If this was not possible the burner was turned at 90 degrees to the light beam reducing the sensitivity by a 90%.

4.2.2 Laboratory Protocols

Washing of Glassware

All used glassware was left to soak in 2% Micro laboratory cleaner solution (International Products Corporation, Cat. No. 6750) for at least 24 hours. The glassware was then rinsed twice with distilled water before drying. Glassware used for reagent solutions, or solutions where the heavy metal concentrations to be determined were likely to very low, was also rinsed twice in double distilled water.

All solutions were made up in double distilled or MilliQ (Millipore Corp., Bedford, MA, USA) reverse osmosis water to avoid the possibility of metal contamination. The conductivity of the water was measured on a regular basis to make sure that it was not contaminated. The extractant solutions were routinely tested for the metals being determined by atomic absorption spectrophotometry.

4.3 Sequential Extraction Scheme

The Tessier extraction scheme was chosen because it is the most widely used and researched sequential extraction scheme. The five fraction extraction scheme allows the analysis of a greater number of samples than more complex nine fraction schemes (e.g. Miller et al., 1983). Investigating a larger number of samples with a well researched and widely used scheme was considered to be more valuable than analysing a smaller number in greater detail with a less widely used fractionation scheme. The use of the Tessier scheme makes comparison of results with other studies possible, although difficult due to the different variations of the scheme used in the various studies of geochemical fractionation.

Sample Treatment and Processing

Six replicates of each sample were analysed. The extractions were carried out in 50 ml centrifuge tubes. One gram of the soil sample was weighed into a centrifuge tube. Two grams of glass beads of 1-2mm diameter were added. The centrifuge tubes were balanced by addition of further glass beads until the six replicates were balanced to allow them to be centrifuged after each extraction. The glass beads were added to ensure adequate mixing of the soil and extractant. This had been a problem during trials of the method; soils with a high clay content would form a pellet during the centrifugation procedure that was almost impossible to re-suspend. Agitation of the samples was achieved by placing the beakers containing the centrifuge tubes on a rotary soil shaker.

To monitor the loss of material, that inevitably occurs during the physical processing of the samples the centrifuge tube, soil and glass beads were weighed before the first extractant was added. After the organic extraction, the centrifuge tubes and content were dried to enable the contents to be transferred to a digestion vessel. The dried centrifuge tube and contents were re-weighed and the loss of material was calculated. With the exception of highly organic surface layers, losses of material were small and are presented in detail in Section 6.2.

The following procedure was repeated after each extraction:

The samples were centrifuged at 6000 rpm in a bench centrifuge. The supernatant from each sample was filtered through a Whatman No. 42 filter paper into a 25ml volumetric flask and made up to volume with 0.1M nitric acid to stabilise the solution until analysis. The solid residue was washed by addition of 8ml of distilled water and agitated for 30 minutes. The residue was recovered by centrifugation for 10 minutes at 6000 rpm and the washings were discarded. The residue was then used in the next extraction.

The scheme used in the present study is a modified version of the Tessier sequential extraction scheme and used five different extractions, these are given below.

- **1 Exchangeable** **1M magnesium chloride (8ml), pH 7**
  - 1 hour, continuous agitation, 20°C

  The process is the exchangeable extraction developed by Tessier et al. (1979).
- **2 Carbonate** **1M sodium acetate (8ml), pH 5**
  - 5 hours, continuous agitation, 20°C

  This extractant is widely used for the removal of the acid extractable phases. The pH of the extractant is critical, a lower pH causes partial dissolution of the amorphous iron and manganese oxides phase.
- **3 Iron and manganese oxides** **0.04M $NH_2OH.HCL$ in 25% acetic acid (20ml)**
  - 6 hours, occasional agitation, 96°C

  The high temperature was maintained by placing the samples in a thermostatically controlled oven. The samples were removed briefly at regular intervals for agitation.
- **4 Organic** **0.02M nitric acid (3ml) + 30% hydrogen peroxide (5ml)**
  - 2 hour, occasional agitation, pH 2, 85°C

  The extraction was carried out in the thermostatically controlled oven in a similar manner to the iron and manganese extraction, but at the lower temperature indicated.
- **Further 3ml hydrogen peroxide pH 2 85°C**
  - 3 hour, occasional agitation, pH 2, 85°C

  A further 3ml of hydrogen peroxide was added and the reaction continued for another 3 hours.
- **Then 3.2M ammonium acetate in 20% nitric acid**
  - 1/2 hour, continuous agitation, 20°C

  This step prevents the readsorption of trace metals on iron oxides. The residue was dried at 105°C for 24 hours and weighed to determine the weight loss during the first four extractions.
- **5 Residual** **Hot Nitric Acid Digest, 10ml Nitric Acid**
  - Reflux the residue for 4 hours in a conical flask

  The digestions were carried out in 100ml conical flasks on a heated sand bed. The samples were not centrifuged, but were filtered through Whatman No. 42 filter paper to remove suspended matter. The filtration was carried out directly into a 25ml volumetric flask diluted to volume with 0.1M nitric acid. The extracts were decanted into 25ml vials.

- **The Sixth Fraction**

  Examination of the results showed that the concentration of iron in the residual fraction was very high. This was interpreted as being caused by the dissolution of crystalline iron which was not removed by hydroxyammonium chloride. In the last set of extractions on the Ringinglow, Site S samples, an extra step was added to the sequence. After the organic extraction the residue was leached for 16 hours with 1M hydrochloric acid, following the method of Huerta-Diaz et al. (1993). The result of this extraction was a partial extraction of crystalline iron reducing the iron content of the residual fraction by approximately 50%.

Analysis of Heavy Metal Content

The extracts were analysed by atomic absorption spectrophotometry for the metals; lead, zinc, copper, cadmium, nickel, iron, and manganese.

4.4 Parallel Extraction Scheme

Samples were extracted independently to determine the various oxide and organic phases present in the soils. The extraction of iron oxides by standard soil chemistry techniques also results in the dissolution of associated heavy metal elements. The resultant solutions were analysed for heavy metals, to obtain an additional set of data on the geochemical fractionation of heavy metal elements in the soils that could be compared with the Tessier extraction scheme.

4.4.1 Determination of Amorphous Iron Oxides

Amorphous iron oxides were determined by extraction with 0.1M sodium pyrophosphate, following the method of Bascomb (1968), see Section 2.2. Sodium pyrophosphate at pH 7 extracts both amorphous aged hydrous oxides and amorphous gel hydrous oxides from soils. Pyrophosphate at pH 10 dissolves only amorphous gel oxides. The pyrophosphate extractant also extracts organic matter from soils. At pH 10 extraction of organic matter is more efficient than at pH 7 (Bascomb, 1968; Schnitzer and Schuppli, 1989a). Pyrophosphate does not remove crystalline oxides of iron. Sodium pyrophosphate extractions at pH 10 and pH 7 were used on samples from the Ringinglow site SRG. On all subsequent extraction only the pH 7 determination was made.

- **Weighing 0.2 g air dried soil into a 50 ml centrifuge tube**

  Six replicates of each sample were determined.

- **Extractant 20 ml 0.1M sodium pyrophosphate pH 7.0 or pH 9.8**

  The sodium pyrophosphate solution was prepared in a 2 litre A-grade volumetric flask. The pH was either left at 9.8, unadjusted, or adjusted to pH 7.0. The adjustment of pH was carried out by the addition of concentrated phosphoric acid, dropwise with agitation, until the pH was reduced to pH 7.0.

  Twenty millilitres of 0.1M sodium pyrophosphate reagent was added to the 0.2g soil sample giving a ratio of extractant to soil of 100:1.

- **Sample agitation**

  The centrifuge tubes were shaken for 16 hours in 600ml beakers on a rotary soil shaker.

- **Centrifugation 6000 rpm, 15 minutes**

  After centrifugation the supernatants were filtered through Whatman No. 42 filter paper into 25ml vials, ready for metal analysis.

- **Metal Analysis**

  The extracts were determined for iron and other heavy metals by atomic absorption spectrophotometry.

4.4.2 Extraction of Humic Substances

A 0.1M sodium hydroxide extraction was used to dissolve soil organic matter. The advantage of this extractant over sodium pyrophosphate is that it does not solubilise the amorphous iron oxide phase. The metal concentrations in organic matter tend to be very low and to obtain sufficient concentrations of trace metal in the extracts, to allow analysis of the metal concentrations, a lower ratio of extractant to soil (25:1) was used than in the sodium pyrophosphate extraction for amorphous iron.

- **Weighing 0.8g air dried soil, 50ml centrifuge tube**

  0.8g of soil was weighed into a 50ml centrifuge tube.

- **Extractant 0.1M sodium hydroxide**

  Twenty millilitres of 0.1M sodium hydroxide solution were added to the soil sample. The soil and extractant were shaken for 16 hours, on a rotary soil shaker.

- **Centrifugation 6000 rpm, 15 minutes**

  The samples were centrifuged to remove solid material and filtered through a Whatman No. 42 filter paper into a 25ml vial.

- **Separation of humic and fulvic acids**

  A 10 ml aliquot of the solution of humic and fulvic acids was placed in a pre-weighed centrifuge tube. After some experimentation, it had been found that the addition of 2ml of 2M hydrochloric acid resulted in the reduction of the solution pH to pH 2 or lower, resulting in the precipitation of humic acid. The humic acid was allowed to coagulate for several hours prior to its removal by centrifugation.

- **Metal determinations**

  The separate fulvic acid fractions and the solutions containing both humic and fulvic acids were air dried and digested in hot concentrated nitric acid, by the method described in Chapter 2. The lead, zinc, copper, nickel, cadmium, iron and manganese concentrations in the fulvic acids and humic extracts were measured by atomic absorption spectrophotometry.

- **Humic acid metal concentrations**

  The metal concentrations in the humic acids were estimated by subtracting the results for fulvic acids from the trace metal concentrations of the humic and fulvic acids solution.

- **Centrifugation 6000 rpm, 15 minutes**

  The humic acid precipitate was dried until constant weight so that a yield could be calculated.

4.5 Soil Organic Matter Extraction and Purification Scheme

This section outlines the method finally adopted and used to obtain the results in these studies. To clarify the rationale behind the procedure, the method steps are given together with the details of why each step was carried out in a particular way.

- **Weighing 5g of air dried soil was placed in a 200ml plastic bottle**

  The extraction was performed on a small sample size so that the volume of solution that needed to be centrifuged was kept to a minimum allowing more samples to be processed. The bottle size was chosen so that they fitted into the centrifuge eliminating the need to transfer solutions after the extraction.

- **Extractant 50ml of 0.1M sodium pyrophosphate**

  The reagent was added to the soil. The volume of extractant was chosen to give a 10:1 ratio of extractant volume to soil weight and is the ratio used in most studies of this type. The concentration of the extractant, 0.1M, was the same as that used in the majority of soil organic matter extraction schemes. Sodium pyrophosphate was chosen to avoid problems of oxidation, and more important in this study, hydrolysis.

- **Atmosphere The air was displaced by nitrogen gas to minimise the oxidation.**

- **Extraction The bottles were shaken on a soil shaker for 24 hours**

  The extraction time chosen was the most common extraction time used in the studies reviewed in Chapter 3. A reciprocal soil shaker was set at a speed sufficient to keep the soil suspended in solution. At the start of the extraction, a high speed was found to be necessary to suspend the soil material, particularly where soils had a high clay content. After the soil had become suspended in the extractant, the speed was reduced to minimise wear and tear on the soil shaker. The samples were checked at regular intervals for the first few hours to make sure the soil remained in suspension.

- **Separation The bottles were centrifuged at 4000 rpm for 30 minutes**

  The highest speed available for 200ml plastic bottles.

- **Filtration Whatman No. 42 filter paper**

  The filtration step was necessary to remove undecomposed plant material that floated on the surface of the supernatant and could not be removed by centrifugation.

- **Centrifugation 6000 rpm for 30 minutes**

  The extracts were centrifuged in 50ml centrifuge tubes. A second centrifugation step was necessary to prevent clogging of the ultra-fine filter membranes.

- **Filtration** **Filter membranes:**
  - Millipore 4.0μm
  - Millipore 0.45μm

  The supernatant from the centrifugation step was immediately filtered through these two filter membranes in sequence. The use of two grades of filter membrane reduced the chance of clogging the ultra-fine 0.45μm Millipore membrane.

- **Precipitation** **Acidification to pH 2.0 by addition of 2M hydrochloric acid**

  All the studies reviewed in Chapter 3 separated the humic and fulvic acid by acidification, which results in the precipitation of humic acid. The solution was acidified to pH 2.0 by addition of 2M hydrochloric acid. In some studies higher concentrations of acid have been used for the acidification step, for example 6M hydrochloric acid (Schnitzer and Schuppli, 1989a). The use of lower concentrations of acid was designed to minimise the displacement of the heavy metals bound to the humic compounds. The acid was added slowly with repeated agitation of the solution to mix the acid and extractant. The pH was monitored with a pH meter, as described in the Section 4.2. The solution was allowed to stand for twenty four hours to allow the humic acid to coagulate.

- **Separation** **Centrifugation at 6000 rpm for 15 minutes**

  Humic and fulvic acids were separated by centrifugation to remove the coagulated humic acid precipitate from the solution of fulvic acid. The centrifugation speed was the one used in the majority of studies in the review. The fulvic acid was purified using XAD-8 resin, this procedure is discussed in the next section.

- **Purification** **Shake Humic Acid with distilled water in a 50ml centrifuge tube**

  Humic acid was washed with dilute acid to remove impurities. The use of distilled water to wash humic acids was found to cause some dissolution of the acid and is best avoided. Washing was carried out by adding 10ml of 0.1M hydrochloric acid to the 50ml centrifuge tube and agitating the pellet into suspension. Stronger acid purification steps were not used, in case these removed metal associated with the humic substances.

- **Recovery** **Centrifugation at 6000 rpm for 15 minutes**

  The humic acid was recovered by centrifugation and the washings were discarded. The washing procedure was repeated twice (previous step and this step). The humic acid

was then moved into a preweighed 100ml conical flask, by dissolution in distilled water. The humic acid was then air dried at 40°C in a thermostatically controlled oven.

- **Humic Acid Yield**

  After the humic acid had been allowed to dry for forty eight hours, the humic acid was weighed until constant weight was obtained.

4.5.1 Purification of Fulvic Acids by Means of XAD-8 Resin

Preparation of Amberlite XAD-Resins

- **Washing** **0.1M sodium hydroxide, followed by distilled water.**

  The resin beads were washed in excess 0.1M sodium hydroxide solution, following the method of Aiken et al. (1979). The resin beads were then rinsed in distilled water (Gregor and Powell, 1986).

- **Soxhlet extraction of XAD-Resin**

  The resin was then placed in a Soxhlet extractor and extracted with acetone for 2 hours, followed by a Soxhlet extraction with methanol for 2 hours (Gregor and Powell, 1986). Previous workers, such as Aiken et el. (1979), used Soxhlet extractions of 24 hour duration. However, in the Gregor and Powell (1986) study, Soxhlet treatments of two hours were found to be sufficient. They also suggested that the additional Soxhlet treatments used by previous workers, such as extracting the resin with dichloromethane and methanol, were unnecessary.

- **Resin storage**

  The beads are stored in methanol until they are required. A 30cm long column was packed using a water-resin slurry. The column was washed with 4 litres of distilled water to remove traces of methanol. The column was then washed with 1 litre of 0.1M hydrochloric acid, followed by 1 litre of 0.1M sodium hydroxide solution. The step was repeated three times. A final treatment of 0.1M hydrochloric acid left the column in the acidic state ready for immediate use. The column was cleaned immediately after use, by allowing 4 litres of 0.1M sodium hydroxide solution to run through it. This step was followed by the three sets of alternate rinses of 0.1M hydrochloric acid and 0.1M sodium hydroxide solution. A further rinse with 1 litre of hydrochloric acid left the column in the acidic state ready for use.

4.5.2 Procedure for the Application of Samples to XAD-8 resin

Sample Preparation

- **Filtration** **0.45μm filtration**

  In the present study, the samples were passed through a 0.45μm filter to separate inorganic material and particular organic matter from soluble organic matter.

Fulvic Acid Processing

- **Sample application, adsorption of fulvic acid onto the column**

  The samples, which had been acidified to pH 2 at an earlier stage in the extraction to remove humic acids by precipitation, were applied to the column at a rate of 12 bed volumes per hour, equivalent to 4ml per minute (Thurman and Malcolm, 1981).

- **Column Washing 200ml 0.1M hydrochloric acid**

  The column was then washed with two void volumes (2 x 100ml) of 0.1M hydrochloric acid and one void volume of 0.01M hydrochloric acid, prior to elution, to remove non humic substances.

- **Elution** **0.1M sodium hydroxide**

  The efficiency of XAD-8 elution of fulvic acid has been found to be 98% (Gregor and Powell, 1986; Aiken et al. 1979). Attempts at eluting fulvic acids using distilled water following the method of Gregor and Powell (1986) did not result in complete elution of fulvic acids, so 0.1M sodium hydroxide was used. The use of a 0.1μm or 0.025μm filtration step to remove a larger proportion of the colloidal material would improve the elution of fulvic acid and allow the elution to be acheived at pH 6.5. However, to acheive this level of filtration with soil extracts would require a much higher centrifugation speed to remove a higher proportion of the colloidal material that otherwise blocks the filter membranes. In the case of natural water samples, fulvic acid is further concentrated by multiple cycling of the humic material through XAD-8 resin (Thurman and Malcolm, 1981; Aiken, 1985). The dilute acid solution of the last rinse step was allowed to drop until it was at the surface of the resin, then a small aliquot of the 0.1M sodium hydroxide eluant was run into the column. The tap of the column was opened slightly to allow the eluant to reach the surface of the resin. The procedure was repeated before the void volume was filled with eluant. The aim of the procedure was to prevent fulvic acid from diffusing into a large volume of eluant in the void volume of the column. After elution, the fulvic acid was contained in a solution of 15ml volume.

- **Yield**

  The fulvic acid was air dried at 40°C in a thermostatically controlled oven and weighed to estimate the yield.

- **Determination of heavy metal content by the digestion of humic and fulvic acids**

  The dried fulvic acids were transferred from the vials to a 100ml conical flask by dissolution in distilled water. A small amount of distilled water was pipetted into the vial containing dried fulvic acid. The vial was shaken until the fulvic acid dissolved and the fulvic acid was then transferred to a 100ml conical flask. The procedure was repeated until all the fulvic acid was transferred to the conical flask. The fulvic acid was then dried, prior to the acid digest, allowing the digestion to be carried out on dry fulvic acid with concentrated nitric acid. The heavy metal contents of the fulvic acids were then determined by atomic absorption spectrophotometry.

  The humic acid, in the 100ml flask, was digested with excess nitric acid. Humic acid is very difficult to digest as it is insoluble in acidic solution and highly recalcitrant. The digestion was complete when the solution turned from brown to colourless. A minimum of ten hours refluxing with concentrated nitric acid was found to be necessary for this digestion.

5 Soil Chemical Properties and Composition

The chemical properties and composition of the four soil types, described in Chapter 4, were determined to characterise the soil profiles and are reported in this chapter. A knowledge of the soil properties: pH, cation exchange capacity, iron oxides composition and organic matter content was considered to be essential for a proper interpretation of the geochemical fractionation results. The correlations between the soil properties are calculated for each soil profile. These correlations are used to determine which combinations of soil properties may be used as 'independent variables' in multiple regression models of the geochemical fractionation of heavy metals.

Chapter 6 describes the geochemical fractionation results at the Hallen and Ringinglow sites and attempts to relate these to the soil properties described in this chapter. The complexation of heavy metals with organic matter, extracted by three different methods, are investigated in relation to the properties of the soil profiles in Chapter 7.

Table 5.1: Summary of Soil Types Found at the Field Sites

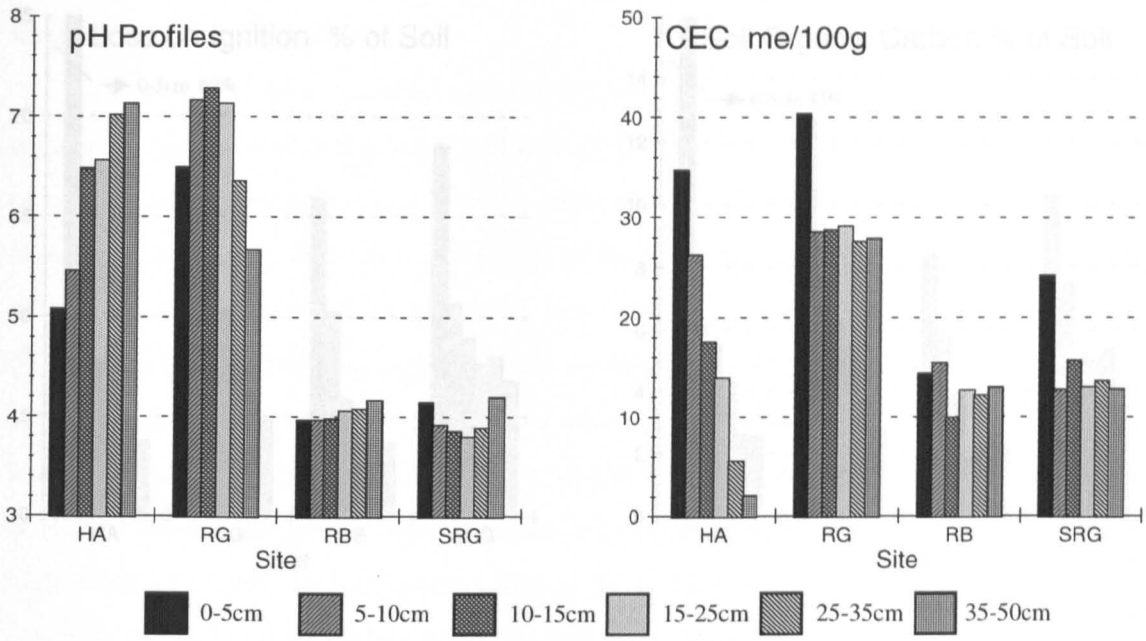
The four soil profiles are described in more detail in Chapter 4 and Appendix 1.

Field Site	Elevation (m)	Vegetation	Soil Type
Site HA, Hallen wood	60	Deciduous woodland	Brown Earth
Site RG, Ringinglow	350	Grassland	Cambic Stagnohumic Gley soil
Site RB, Ringinglow	290	Heather	Ironpan Stagnohumic Podzol
Site SRG, Ringinglow	300	Deciduous woodland	Typical Brown Earth

5.1 Soil pH

Soil pH is an important soil property controlling the speciation of heavy metals in soils and sediments, by competition between hydrogen ions and heavy metal cations. The graph of soil pH, at the different depths in the soil profiles studied (Figure 5.1), shows similar pH profiles for the two acidic soil profiles sites RB, an acid podzol, and SRG, a brown earth. Both soils are acidic with a pH of around 4 at all depths in the profile, reflecting the noncalcareous substrate (millstone grit). The pH profile at Berwick Ridge, Hallen, site HA, a brown earth, reflects the deposition of nitric and sulphuric acids from the industrial complex at Avonmouth. Acid deposition results in acidification of the upper layers of the soil profile. The lower depths in the soil profile remained neutral. The result was a profile with pH increasing with depth

Figure 5.1 pH and Cation Exchange Capacity The graphs illustrate the results of pH and cation exchange capacity determinations (y-axis) at each of the four sites. The histogram bars are plotted in groups of six depicting the soil property (mean 6 replicates) at increasing depth in the soil profiles (x-axis).

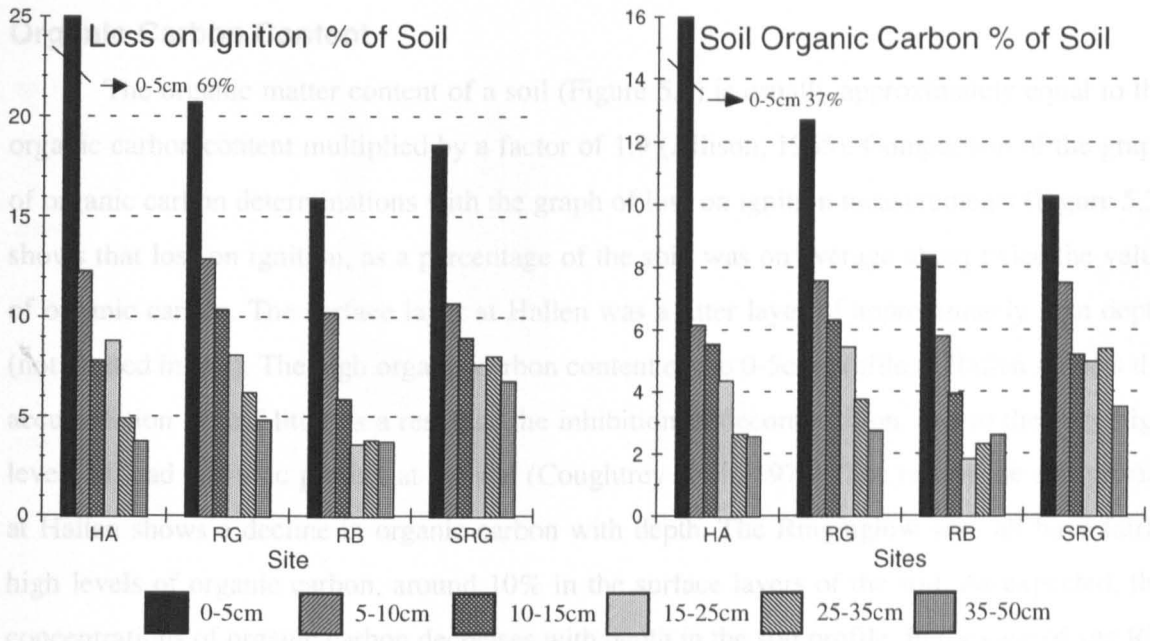


from pH 5 at the surface to pH 7 in the 35-50cm profile. The pH profile of site RG, a stagnogley soil, also shows significant changes in pH with depth. The pH increases down the first 3 stages and then becomes more acidic with depth (Figure 5.1).

5.2 Cation Exchange Capacity

Cation exchange capacity was determined to estimate the potential size of the exchangeable fraction. The graph of cation exchange capacity for the different sites (Figure 5.1) shows that the only site where there are significant changes down the soil profile was site HA, the brown earth from Hallen. At Hallen, cation exchange capacity decreased with depth in the soil profile despite the pH change from acidic to neutral (Figure 5.1). Cation exchange capacity is controlled by the number of available exchange sites on clay, other minerals and organic matter. The decreasing concentration of organic matter down a soil profile reduces the contribution of organic matter to cation exchange capacity. However, mineral components, such as clays, tend to become more abundant down profile increasing their contribution to cation exchange capacity. The balance between the contributions of clay minerals and organic matter is the main factor controlling the cation exchange capacity of the soil. Cation exchange capacity at the Ringinglow sites was found to be relatively constant with depth in the profile.

Figure 5.2 Loss on Ignition and Organic Carbon Content The graphs illustrate the results of these determinations (y-axis) at each of the four sites. The histogram bars are plotted in groups of six depicting the soil property (mean 6 replicates) at increasing depth in the soil profiles (x-axis).



5.3 Organic Matter Determinations

Organic matter was determined by two approaches; loss on ignition and a determination of organic carbon content. The loss on ignition determinations allow an independent estimate of the soil organic matter content, confirming results obtained by the determination of organic carbon content. To allow the changes in organic matter concentrations down the soil profile to be displayed graphically the 0-5cm profile at Hallen is not plotted in full in Figures 5.2. A number of studies have compared loss on ignition determinations with organic carbon estimates for different soil types (e.g. Howard, 1972). However, a much larger sample of different soils than was examined here would be needed to investigate soil type specific differences between these estimates of organic matter.

Loss On Ignition

The loss on ignition determinations (Figure 5.2) measure the weight loss after the combustion of organic matter at 375°C for 18 hours. However, other factors influence loss on ignition, including decomposition of carbonates and changes in the water content. The weighing protocol, described in Chapter 4, was designed to standardise the water content of the samples before and after the determination. The aim of the procedure was to keep the contribution of changes in water content to changes in weight to a minimum. Decomposition

of carbonates is unlikely at the temperature used for the determination (375°C), but would be important if the procedure was applied to alkaline soils. The soils investigated were all neutral to acidic, so the carbonate contents were unlikely to be high.

Organic Carbon Content

The organic matter content of a soil (Figure 5.2) is usually approximately equal to the organic carbon content multiplied by a factor of 1.9 (Allison, 1965). Comparison of the graph of organic carbon determinations with the graph of loss on ignition measurements (Figure 5.2) shows that loss on ignition, as a percentage of the soil, was on average about twice the value of organic carbon. The surface layer at Hallen was a litter layer of approximately 5cm depth (not plotted in full). The high organic carbon content of the 0-5cm profile at Hallen reflects the accumulation of leaf litter as a result of the inhibition of decomposition, due to the very high levels of lead and zinc present at the site (Coughtrey et al., 1979). The rest of the soil profile at Hallen shows a decline in organic carbon with depth. The Ringinglow sites all have fairly high levels of organic carbon, around 10% in the surface layers of the soil. As expected, the concentrations of organic carbon decreases with depth in the soil profile. In the case of site RB there is an increase in the organic carbon content of the soil in the 15-25cm, 25-35cm and 35-50cm profiles, which is probably due to organic matter accumulation at these depths.

5.4 Iron Oxides

To clarify the types of iron oxide extracted by the sequential extraction, iron and manganese oxides, organic and residual extractions, amorphous iron oxides present in the soil profile were estimated by pyrophosphate extraction, a standard soil technique. Amorphous iron was operationally defined as the iron extracted by a pH 7 pyrophosphate extraction, after Bascomb (1968). The techniques for the iron determinations are described in Chapter 4. Iron concentrations were determined in:

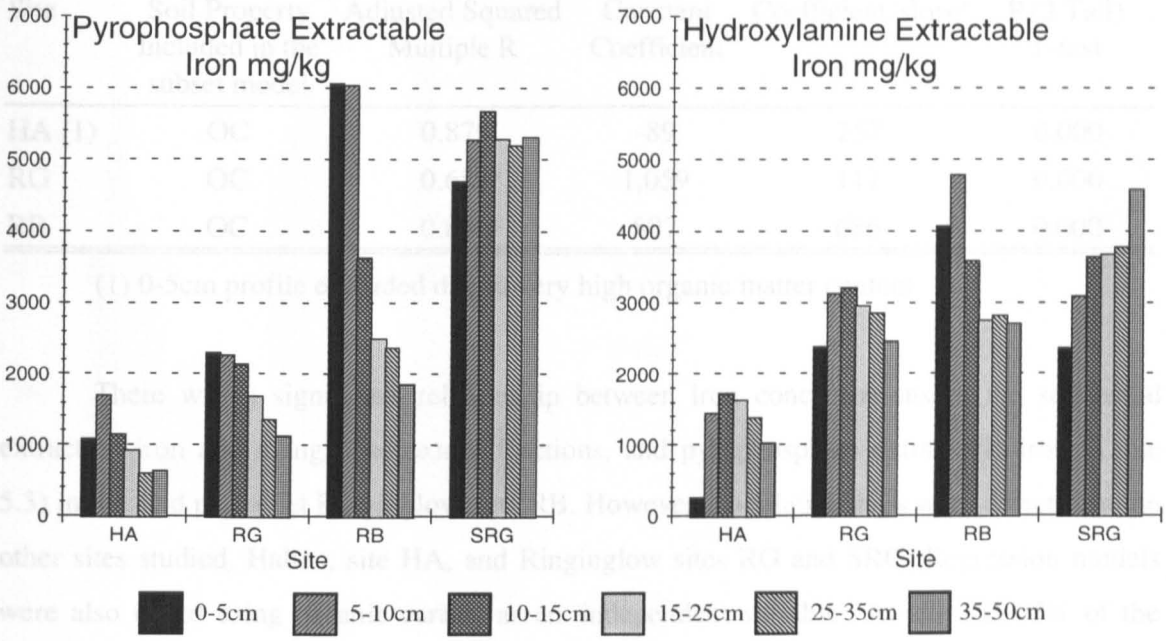
(i) extracts obtained at each stage of the sequential extraction scheme,

(ii) a pyrophosphate extraction for amorphous iron,

(iii) the total digestion of the soil samples.

These results were then related to the iron concentrations in the iron and manganese oxides fraction extracted by the hydroxylamine extraction of the sequential extraction scheme, described in Chapter 2. In general iron concentrations in the sequentially extracted organic matter phase were of a similar level to those in the iron and manganese oxides phase. The highest concentrations of iron were found in the residual digestion.

Figure 5.3 Pyrophosphate and Hydroxylamine Extractable Iron The graphs illustrate the results of these determinations at each site (x-axis). Hydroxylamine is used in the sequential extraction scheme to remove the oxide occluded phase. Histogram bars are plotted in groups of six depicting the soil property (mean 6 replicates) at increasing depth in the soil profiles.



Amorphous Iron

The graph of pyrophosphate extractable iron at different depths in the soil profile at each site illustrates comparatively low concentrations of amorphous iron in the Hallen soil compared to the soils from Ringinglow (Figure 5.3). At three of the sites, HA, RG, and RB pyrophosphate extractable iron decreased with depth in the soil profile. However, at site SRG, an acidic brown earth profile, there was little change in the concentration of amorphous iron extracted with depth. The graph of hydroxylamine extractable iron (Figure 5.3) shows lower concentrations of iron in the top soil profile, compared to the pyrophosphate extraction. As pyrophosphate extracts some organic matter at pH 7, the higher concentrations of pyrophosphate extractable iron relative to hydroxylamine extractable iron, in the upper soil profiles, could be due to the higher concentrations of organic matter at these soil depths. An alternative explanation would be that the hydroxylamine, unlike pyrophosphate, was unable to extract amorphous iron associated with organic matter. The results of the chemical extractions do not yield enough information to allow a distinction to be made between these two possible hypotheses. Regression analysis showed a highly significant relationship between pyrophosphate extractable iron and organic carbon content at sites HA and RB, and a significant but weaker relationship at site RG (Table 5.2).

Table 5.2: Summary of Regression Analysis

Regression Model: PyrFe = Constant + OC n=36

PyrFE - Pyrophosphate pH 7 extractable iron OC - Organic Carbon

Site	Soil Property Included in the subset model	Adjusted Squared Multiple R	Constant Coefficient	Coefficient 'slope'	P (2 Tail) T-test
HA (1)	OC	0.879	-89	257	0.000
RG	OC	0.687	1,059	117	0.000
RB	OC	0.850	897	686	0.000

(1) 0-5cm profile excluded due to very high organic matter content.

There was a significant relationship between iron concentrations in the sequential extraction iron and manganese oxides fractions, and pyrophosphate extractable iron (Table 5.3) in the acid podzol at Ringinglow, site RB. However, no relationships were detected at the other sites studied, Hallen, site HA, and Ringinglow sites RG and SRG. Regression models were also tested using organic carbon as an 'independent variable'. At site RB 93% of the variance in the iron content of the iron and manganese oxides phase was accounted for by organic carbon and pyrophosphate extractable iron. Organic carbon was also found to be an important factor at site SRG. No association was detected between iron in the iron and manganese oxides phase at Hallen, site HA, and amorphous iron or organic carbon content.

Table 5.3: Summary of Regression Analysis

Regression Models: FeMnO [Fe] = Constant + PyrFe n=36

FeMnO [Fe] = Constant + OC + PyrFe n=36

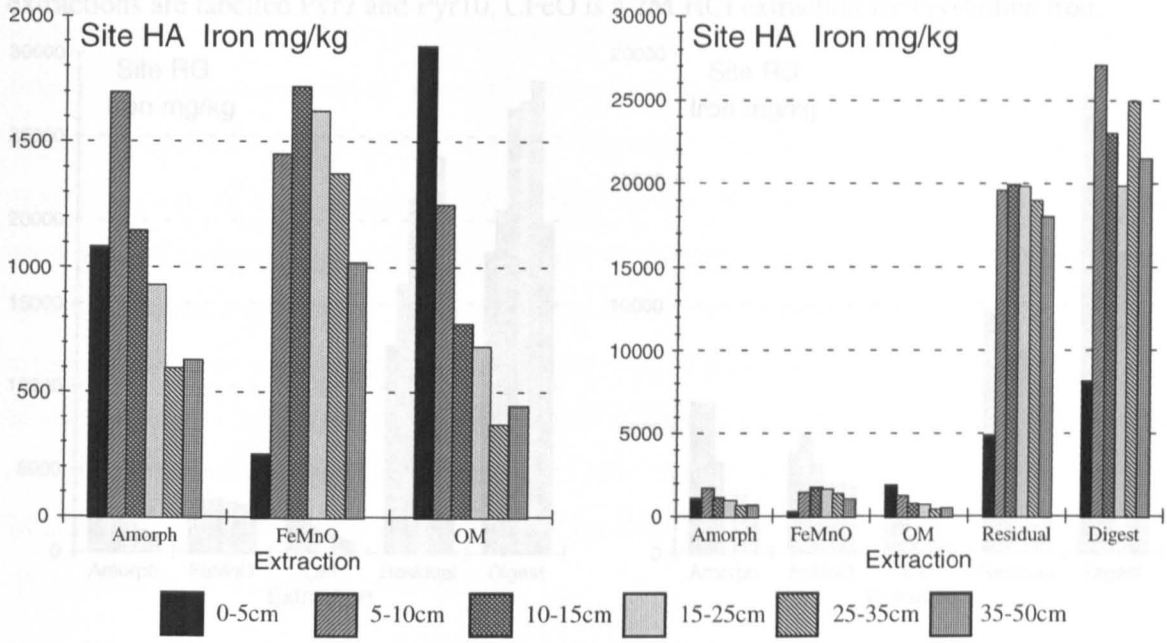
FeMnO [Fe] is the iron concentration in the iron and manganese oxides fraction.

Site	Soil Property Included in the subset model	Adjusted Squared Multiple R	Constant Coefficient	Coefficient 'slope'	P (2 Tail) T-test
RB	PyrFe	89.7	1,840	0.431	0.000
	OC, PyrFe	92.6	1,760	OC: -155 PyrFe: 0.625	0.000 0.000
SRG	OC	90.6	5,353	OC: -299	0.000

Comparison of Iron Extractions At Hallen and Ringinglow

The results of the various extractions of iron oxides are plotted in Figure 5.4. To allow the comparison of much lower concentrations of iron in the amorphous, iron and manganese

Figure 5.4 Iron concentrations at Hallen, site HA: (i) pyrophosphate pH 7 extractable (Amorph); (ii) sequential extraction iron and manganese oxides (FeMnO), organic matter (OM) and residual fractions; and (iii) nitric acid digestion. Histogram bars (mean 6 replicates) are plotted in groups of six, by extraction, at increasing depth in the soil profiles.



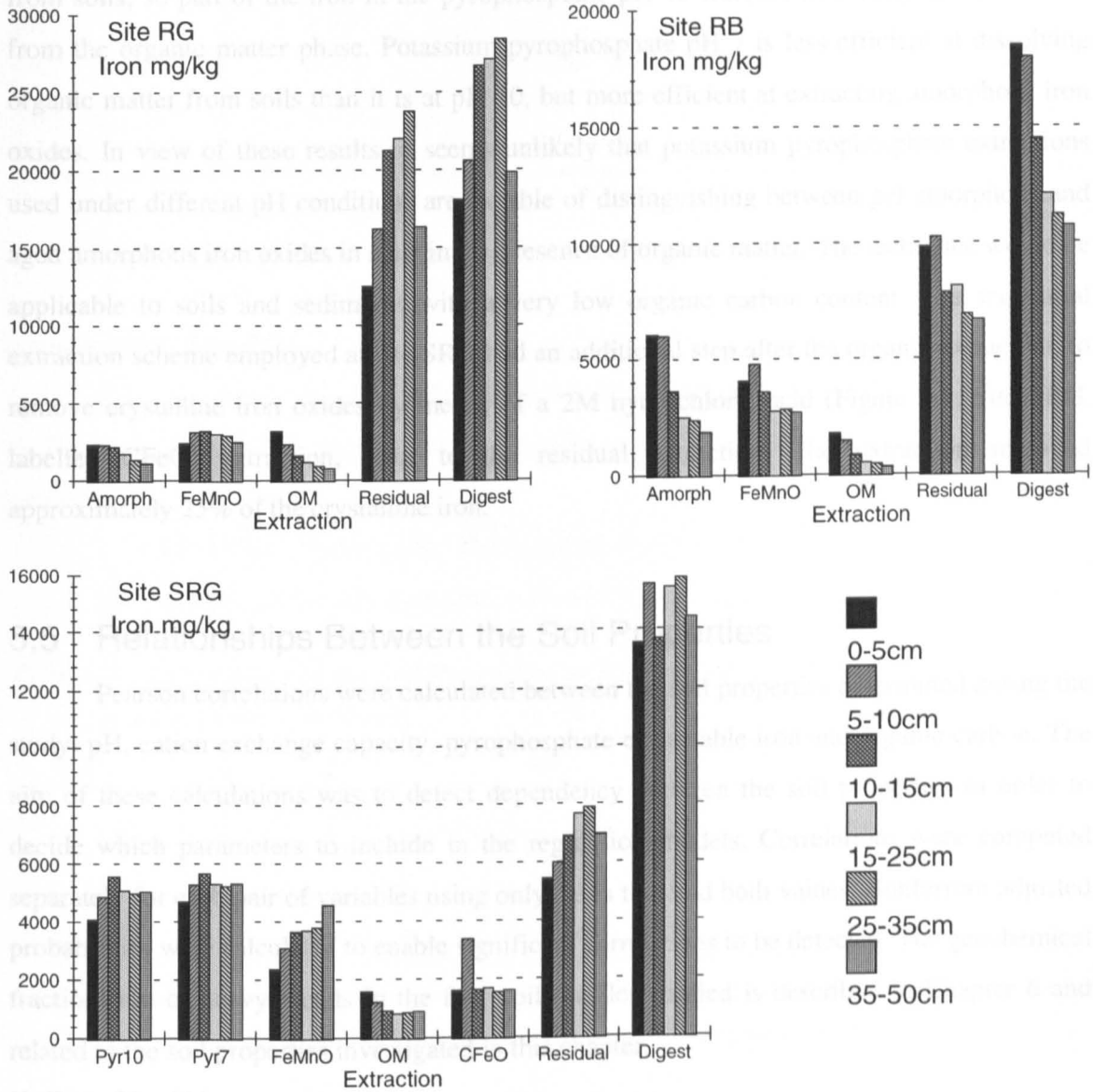
oxides and organic matter phases, the same data is also plotted without the residual and total digest concentrations (Figure 5.4).

The high proportion of iron in the residual phase of the sequential extraction scheme in the brown earth profile at Hallen suggests that the majority of the iron oxides were present in crystalline form. There was a reasonable similarity in the concentrations of iron extracted by the pyrophosphate and hydroxylamine extractions. These results suggest that the hydroxylamine hydrochloride extraction procedure extracts amorphous iron oxides, but leaves crystalline iron oxides which are extracted in the residual fraction. The high concentrations of iron in the organic matter fractions suggest that the organic phase was strongly associated with iron oxides.

At Ringinglow site RG, a neutral stagnogley, iron levels in the residual fraction and the total digestion were found to be between five and ten times higher than those in the amorphous, iron and manganese oxides fraction, and organic bound fractions (Figure 5.5) Site RG). These results indicate that the majority of the iron was present in crystalline form, which was only removable by strong acids.

Iron at Ringinglow site RB, an acid podzol, was more evenly distributed between the amorphous and crystalline forms than in the brown earth at Hallen, site HA and the neutral

Figure 5.5 Iron concentrations at Ringinglow: (i) pyrophosphate pH 7 (Amorph); (ii) sequential extraction iron and manganese oxides (FeMnO), organic (OM) and residual fractions; and (iii) nitric acid digest. Histogram bars (mean 6 replicates) are plotted in groups of six, by extraction, at increasing depth in the soil profiles. For site SRG the pyrophosphate extractions are labelled Pyr7 and Pyr10, CFeO is a 2M HCl extraction for crystalline iron.



stagnogley at Ringinglow, site RG (Figure 5.5 Site RB). There was less iron associated with the organic matter phase than at the other sites. The concentrations of iron in all phases decreased with depth in the soil profile.

Soil samples from the Ringinglow site SRG, a brown earth, were extracted by potassium pyrophosphate, at pH 7 to remove aged amorphous oxides and at pH 10 to extract gel amorphous oxides, following the method proposed by Bascomb (1968). The results were expected to show that higher concentrations of iron were extracted by the pH 7

pyrophosphate extraction than by the pH 10 extraction. The results of these extractions showed that the two reagents extracted very similar quantities of iron (Figure 5.5 Site SRG). However, potassium pyrophosphate at pH 10 is also an effective extractant of organic matter from soils, so part of the iron in the pyrophosphate pH 10 fraction was likely to have arisen from the organic matter phase. Potassium pyrophosphate pH 7 is less efficient at dissolving organic matter from soils than it is at pH 10, but more efficient at extracting amorphous iron oxides. In view of these results, it seems unlikely that potassium pyrophosphate extractions used under different pH conditions are capable of distinguishing between gel amorphous and aged amorphous iron oxides in soils in the presence of organic matter. The technique would be applicable to soils and sediments with a very low organic carbon content. The sequential extraction scheme employed at site SRG had an additional step after the organic extraction, to remove crystalline iron oxides by means of a 2M hydrochloric acid (Figure 5.5, Site SRG, labelled CFeO) extraction, prior to the residual extraction. The extraction removed approximately 25% of the crystalline iron.

5.5 Relationships Between the Soil Properties

Pearson correlations were calculated between the soil properties determined during the study: pH, cation exchange capacity, pyrophosphate extractable iron and organic carbon. The aim of these calculations was to detect dependency between the soil properties in order to decide which parameters to include in the regression models. Correlations were computed separately for each pair of variables using only cases that had both values. Bonferroni adjusted probabilities were calculated to enable significant correlations to be detected. The geochemical fractionation of heavy metals in the four soil profiles studied is described in Chapter 6 and related to the soil properties investigated in this chapter.

Hallen, Site HA

The results of correlation analysis of the soil chemical properties and composition in the brown earth at Hallen, site HA, (Table 5.4) showed highly significant correlations between all four soil properties. In view of these results, the regression models described in Chapter 6 will be restricted to using a single soil property as an independent variable. The clear trend in pH at Hallen, increasing from pH 5 to pH 7.2 (Figure 5.1) down the soil profile, provides an opportunity to investigate the influence of pH on the geochemical fractionation of heavy metals in the soil profile.

Table 5.4: Correlation Analysis of the Soil Properties at Hallen, Site HA

Pearson Correlation Matrix: Omitting profile 1, 0-5cm. n=30

OC - Organic Carbon, PyrFe - Pyrophosphate pH7 extractable iron.

	pH	OC	CEC	PyrFe
pH	1.000			
OC	-0.899	1.000		
CEC	-0.95	0.967	1.000	
PyrFe	-0.978	0.94	0.96	1.000

Bartlett Chi-Square Statistic: 276.158 DF=6 PROB=0.000

All the correlations are significant at the 99% confidence level.

Ringinglow, Site RG

Table 5.5 shows the correlations between the soil properties in the neutral stagnogley at Ringinglow, site RG. Significant correlations were found between the following soil properties:

CEC x OM, PyrFe x pH, PyrFe x OM, PyrFe x CEC.

pH was not significantly associated with cation exchange capacity and organic carbon.

Table 5.5: Correlation of the Soil Properties at Ringinglow, Site RG

Pearson Correlation Matrix n=36

	pH	OC	CEC	PyrFe
pH	1.000			
OC	N.S. 0.309	1.000		
CEC	N.S. -0.059	0.894	1.000	
PyrFe	0.709	0.834	0.534	1.000

All the correlations were found to be significant at the 99% level, except those labelled N.S.

Bartlett Chi-Square Statistic: 183.931 DF=6 PROB=0.000

Ringinglow, Site RB

Table 5.6 shows the correlations between the soil properties in the acid podzol at Ringinglow, site RB. There were significant correlations between the following properties:

pH x PyrFe, OC x pH, OC x CEC, OC x PyrFe, CEC x PyrFe.

Correlations were found to be significant at the 99% level except OCxCEC which was significant at the 95% confidence level. Correlations labelled N.S. were not significant.

pH and cation exchange capacity were not significantly associated.

Table 5.6: Correlation of the Soil Properties at Ringinglow, Site RB

Pearson Correlation Matrix n=36

	pH	OC	CEC	PyrFe
pH	1.000			
OC	-0.644	1.000		
CEC	N.S. -0.139	0.441	1.000	
PyrFe	-0.752	0.925	0.501	1.000

Bartlett Chi-Square Statistic: 108.731 Df=6 Prob=0.000 N=36

Ringinglow, Site SRG

The correlations between the soil properties in the acidic brown earth at Ringinglow, site SRG, are described in Table 5.7, the following properties were found to be significantly associated:

PyrFe x CEC, OM x CEC, OM x PyrFe

Table 5.7: Correlation of the Soil Properties at Ringinglow, Site SRG

Pearson Correlation Matrix n=36

	pH	OC	CEC	PyrFe
pH	1.000			
OC	N.S. 0.197	1.000		
CEC	N.S. 0.358	0.765	1.000	
PyrFe	N.S. -0.352	-0.622	-0.571	1.000

All the correlations were found to be significant except those labelled N.S.

Bartlett Chi-Square Statistic: 54.470 DF=6 PROB=0.000

The cation exchange capacity at site RG was found to be constant, irrespective of depth in the soil profile. At site RB both cation exchange capacity and pH remained constant with increasing depth in the soil profile and at site SRG only organic carbon content varied with depth. These results, together with the Pearson correlations, demonstrate that in most cases the regression models relating the geochemical fractionation of heavy metals in these soil profiles will be restricted to a single soil parameter as the independent variable.

The soil properties determined in the soil profiles show large differences between the four different soil types examined. The cation exchange capacity of the soil profiles was approximately constant with depth in the soil profile at the three Ringinglow sites. However, there was a significant decrease in cation exchange capacity with increasing depth in the brown

earth profile at Hallen. As anticipated, organic carbon concentrations decreased with depth in each of the soil profiles examined. Organic carbon concentrations were found to decrease steadily with depth in both the brown earth profile from Hallen and the stagnogley profile from site RG. In the acid podzol, site RB and the acidic brown earth, site SRG, the organic carbon content decreased in the top layers of the soil, but became stable or increased at lower depths. The results of the iron oxide extractions demonstrated that the iron and manganese oxides extraction of the sequential extraction scheme selectively removes amorphous iron oxides and was insufficiently powerful to remove crystalline iron oxides. The majority of the iron oxides were shown to be in crystalline form in all three soil profiles examined.

The pH of the neutral stagnogley at Ringinglow, site RG, which was approximately pH 6, differed significantly from the acid podzol at site RB and the acidic brown earth at site SRG, which were both approximately pH 4. As pH is a logarithmic scale, these soil profiles had hydrogen ion concentrations that differed by a factor of 100. In the brown earth soil profile at Hallen, the pH increased from pH 5 in the surface layer to pH 7 in the 35-50cm depth, a similar change in hydrogen ion concentrations to that found between the different soil profiles at Ringinglow. Such a large difference in the hydrogen ion concentration, as exists between the soils at Ringinglow, or within the soil profile at Hallen, was expected to have a marked effect on the geochemical fractionation of the heavy metals in the soil profiles and is discussed in Chapter 6.

6 Geochemical Fractionation of Heavy Metals In Soil Profiles

6.1 Interpretation of the Sequential Extraction Results

Sequential extractions were used to estimate heavy metals concentrations associated with soil components and geochemical phases. The development and operation of these schemes was reviewed in section 2.1. Comparison of the geochemical fractionation of heavy metals in soils with the size and nature of the soil phases should provide valuable insights into the processes that control metal availability in soils.

There are two concepts that are important in the interpretation of sequential extraction results:

(i) the affinities of a single heavy metal, such as lead, for the various geochemical phases present in soils.

(ii) competition between metals for binding sites on specific substrates, such as cation exchange sites, or organic matter complexes.

The first concept has been addressed by the majority of sequential extraction studies, which describe the distribution of heavy metals between the various geochemical phases in soils. The second concept is important where there are two or more metals competing for a limited number of binding sites on a substrate, such as cation exchange sites or inner sphere complexation on organic matter.

Analysis of the Results

The geochemical fractionation of lead, zinc, cadmium, and copper at Hallen is described and related to the chemical properties and composition of the soil profile. The Ringinglow study investigated the effect of soil type on the speciation of heavy metals. At Ringinglow the geochemical fractionation of each metal was compared in the three soil types investigated. In Chapter 7 the results of the organic matter extractions are described and compared to the sequential extraction results. The details of the four sites investigated, using the sequential extraction scheme, are summarised in Table 5.1.

The complexity and quantity of data produced by sequential extraction studies makes examination of the results difficult. Graphical depiction of the results provides a much clearer presentation of the data than numerical tables. In this chapter the absolute concentrations of metal in the different geochemical fractions are illustrated in bar graphs for each depth in the soil profile. The relative sizes of the different fractions associated with a single metal are

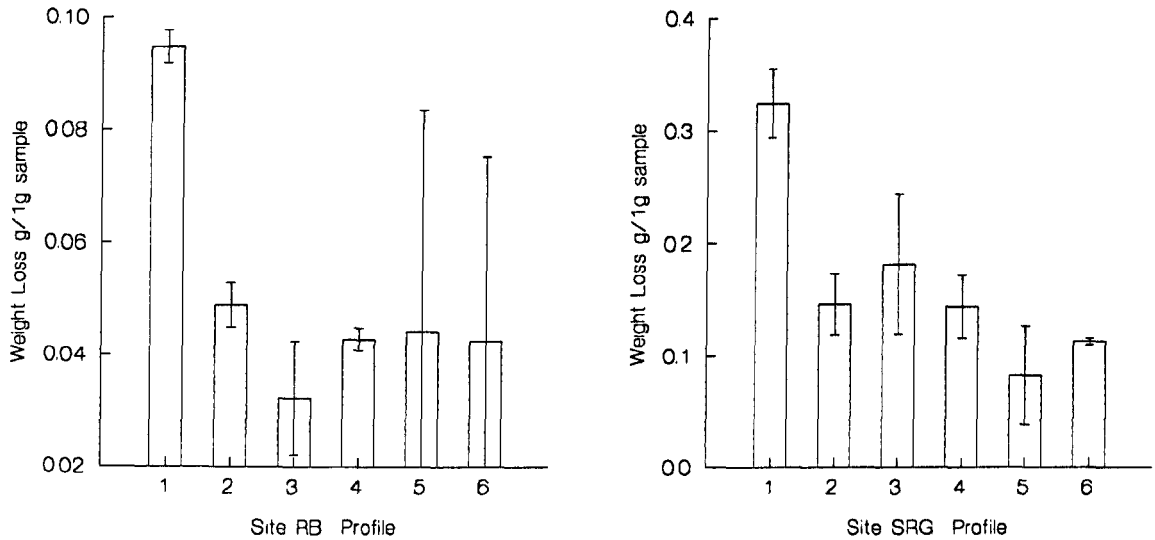
illustrated in 100% stacked bar graphs. The acid extractable fraction is labelled as the carbonate fraction to keep the graph legends at a reasonable size. It is clear that the pH 5 acetic acid extraction extracts some hydroxide bound metal as well as carbonates. Available metal is defined as the sum of the exchangeable and acid extractable fractions. The metal concentrations in each fraction for each soil are listed in Appendix 3.

Statistical Analysis

The statistical analysis attempts to relate changes in the geochemical fractionation of the heavy metals in the soil profiles to changes in soil composition and properties with increasing depth. The soil properties chosen for the regression analysis were those that were expected to be associated with the particular phase being investigated. Metals associated with the cation exchangeable phase of the sequential extraction scheme were expected to be related to the cation exchange capacity of the soil. As organic matter provides a large number of cation exchange sites, the inclusion of organic matter in the regression models for exchangeable metal was also attempted. The relationship between the heavy metal content of the iron and manganese oxides fraction and the amorphous iron content of the soil samples was investigated. Finally, the concentration of heavy metals in the organic phase was expected to be related to the organic matter content of the soil, so this interaction was tested in a regression model. Some of the soil components are interlinked. Iron oxides are closely associated with organic matter, so the models also test the organic matter component against the heavy metal concentrations in the iron and manganese oxides phase.

Multivariate regression analysis was used to investigate relationships between the geochemical fractionation of heavy metals and soil properties. The correlations between the soil properties at each site were determined in Chapter 5 (Tables 5.4-5.7). The variables for inclusion in the models were chosen to avoid having soil properties that were highly dependent on each other, avoiding problems of multicollinearity within the 'independent' variables. The results reported are the adjusted square multiple R, which is the percentage of the variation in the metal fraction that was associated with the particular soil properties indicated in the model, and the coefficient predicted by the model. The equations produced by the model were not used, as they imply a simple linear relationship between the metal in the geochemical fraction and the soil properties. In most cases the relationship is very unlikely to be linear, and there is insufficient data to justify that type of approach. The tests were used to simply determine the percentage of the variation attributable to the soil properties included in the model. The

Figure 6.1 Weight Loss During the Sequential Extraction Procedure at Ringinglow: Each graph represents the mean and standard error (6 replicates) of the weight loss, which is plotted in g/1g sample on the y-axes. The graphs have different y-axis scales. Profiles are numbered as follows, 1=0-5cm, 2=5-10cm, 3=10-15cm, 4=15-25cm, 5=25-35cm and 6=35-50cm.

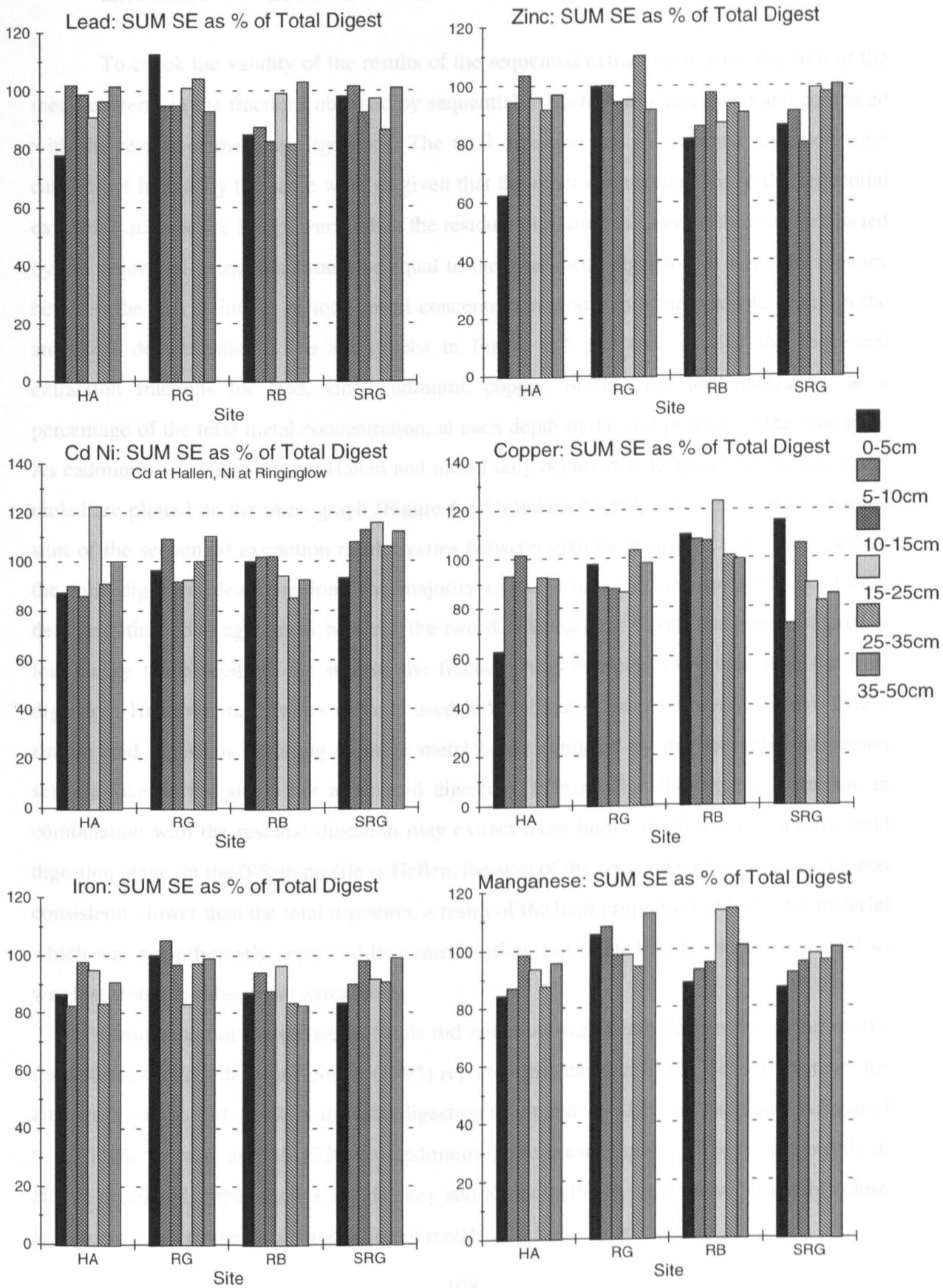


regression results were checked by examination of the graphs of the residuals from the statistical test.

6.2 Mass Loss During The Sequential Extraction Procedure

The sequential extraction technique involves physical processes, such as centrifugation, which result in the loss of some soil material at each extraction stage. An assessment was made of the soil lost during the entire extraction procedure using samples from Ringinglow, sites RB and SRG. Samples were weighed before and after extraction as described in the sequential extraction section of Chapter 4. Figure 6.1 illustrates the loss of soil material during the sequential extraction procedure as a proportion of the initial sample weight (1g) for each soil profile at Ringinglow, sites RB and SRG. The losses of material at site RB, were quite small, usually less than 0.05g or 5%. However, larger losses occurred in the 0-5cm litter layer where organic matter, which had a lower density than water, was not separated by centrifugation and was lost to subsequent extractions. Losses of material at site SRG were considerably larger than those for site RB (Figure 6.1). The sequential extraction scheme used at site SRG included an extra extraction step prior to the residual digestion, which may explain the larger estimate of material lost during the extraction. The procedure is a useful cross check, if there are large differences between the sum of the fractions and the results of a total digestion it may indicate errors in the determinations.

Figure 6.2 Sum of the Sequential Extraction Fractions Versus Total Digestions: The sum of the concentrations of a metal in the sequential extraction fractions plotted as a percentage of the result obtained by total digestion. Histogram bars are plotted in groups of six depicting the percentages (mean of 6 replicates) at increasing depth in each of the soil profiles.

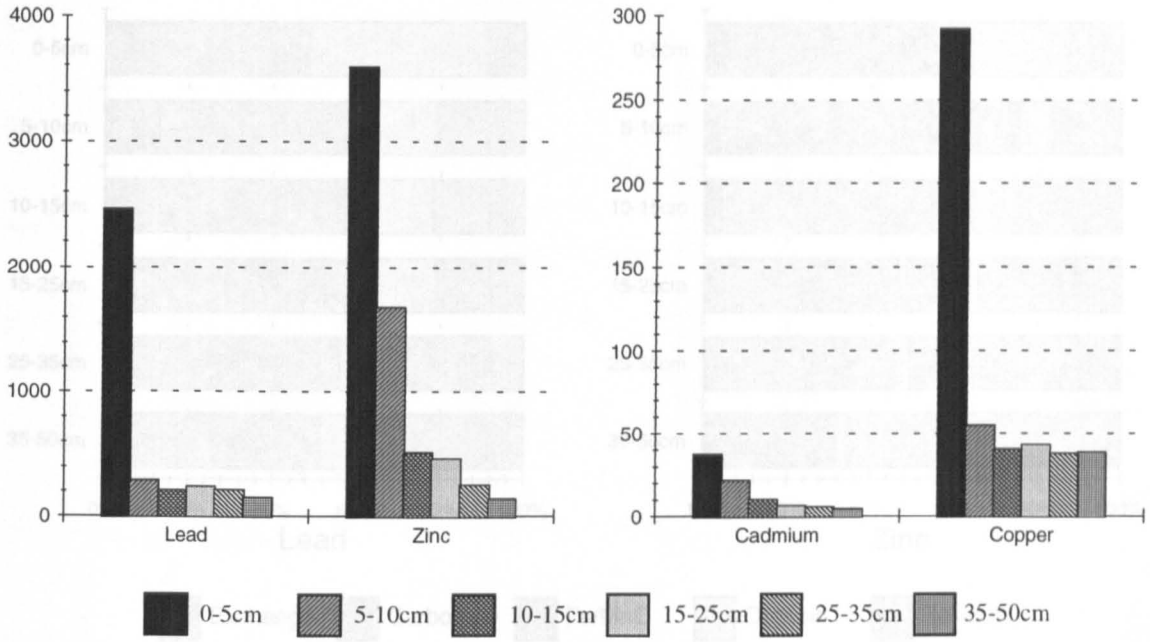


6.3 Sum of the Heavy Metal Concentrations in: Sequential Extraction Fractions Versus Total Digestion

To check the validity of the results of the sequential extraction scheme the sum of the metal contents in the fractions obtained by sequential extraction was calculated and compared with the results of the total digestions. The total digestion and the residual digestion were carried out in exactly the same way, so given that the other extractants used in the sequential extraction scheme are less powerful than the residual digestion, the sum of the metal extracted by the sequential extraction should be equal to the total metal digestion. A large discrepancy between the two estimates of total metal concentration would indicate possible errors in the analytical determinations. The six graphs in Figure 6.2 plot the sums of the sequential extraction fractions for lead, zinc, cadmium, copper, nickel, iron and manganese as a percentage of the total metal concentration, at each depth in the soil profiles of the four sites. As cadmium was found only at Hallen and nickel only occurred at Ringinglow, cadmium and nickel are plotted on the same graph (Figure 6.2 Cadmium Nickel). The results show that the sum of the sequential extraction results varies between extreme values of 62% and 124% of the total digestion determination. The majority of the results lie between 80% and 110%, demonstrating good agreement between the two determinations. Given that some material is lost during the procedure, the sum of the fractions was expected to be less than the total digestion. However, the five extractants used in combination may be more effective than a simple acid digestion, resulting in more metal being extracted by the sequential extraction scheme than by the single hot nitric acid digestion. In particular, the organic extraction in combination with the residual digestion may extract more humic materials than a nitric acid digestion alone. In the 0-5cm profile at Hallen, the sum of the sequential extraction results was consistently lower than the total digestion, a result of the high proportion of leaf litter material which was not efficiently separated by centrifugation, but floated on the supernatant and so was lost from the subsequent extractions.

Comparison of the different metals did not show significant differences in the results for different metals. Jeng and Singh (1993) reported that the sum of the Tessier fractions for zinc was equal to 114-124% of the total digestion result and 97-117% for cadmium, compared to 80-110% for zinc and 85-122% for cadmium in the present study, if the 0-5cm profile at Hallen is omitted. Other studies, e.g. Hickey and Kittrick (1984), have found reasonably close agreement between the results for different metals.

Figure 6.3 Total Digestion of Heavy Metals at Hallen: Each graph represents the total metal concentrations at a site plotted in mg/kg on the y-axis. These determined were made by hot nitric acid digestion. The histogram bars are plotted in groups of six depicting the metal concentrations (mean of 6 replicates) at increasing depth in the soil profile.



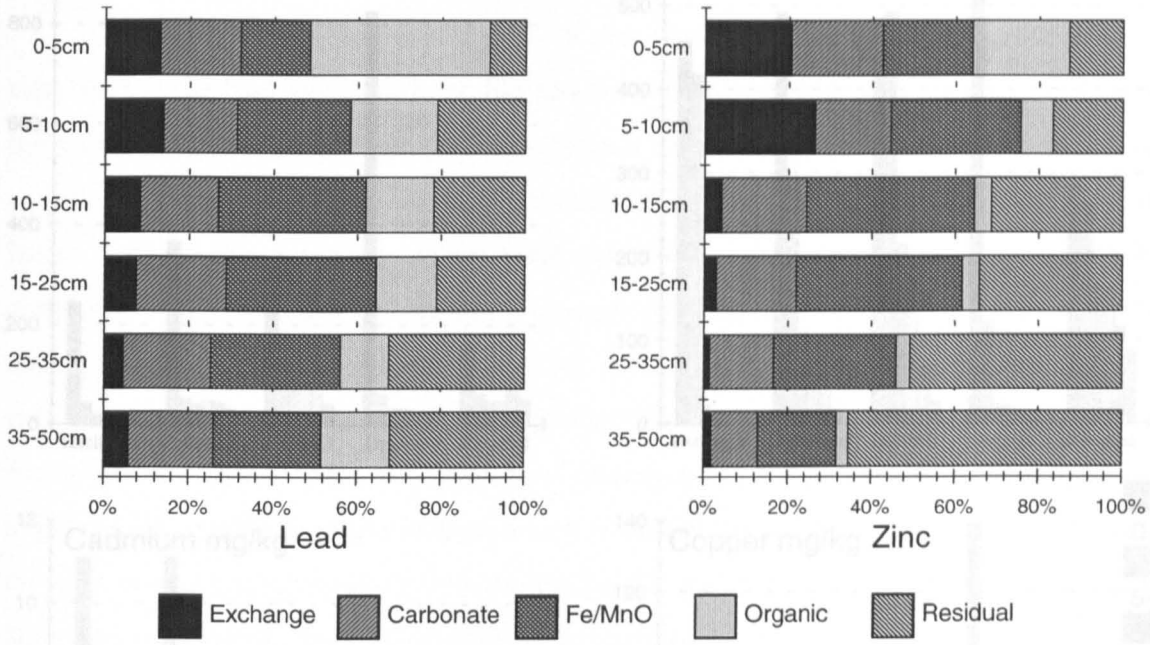
6.4 Total Digestion Results: Berwick Ridge, Hallen

Total metal concentrations were determined at each depth in the soil profile, by hot nitric acid digestion. At site HA, a brown earth (Table 6.1), lead and zinc were present at very high concentrations, 3500mg/kg in the surface layer of the soil, due to the proximity of the Avonmouth lead/zinc smelter (Figure 6.3). Cadmium and copper were also present in the ore smelted and these were found at the site in significant concentrations (Figure 6.3). Very high concentrations of copper and lead were present in the 0-5cm profile, with relatively constant and much lower concentrations below the litter layer. Cadmium and zinc concentrations decreased steadily with depth in the soil profile (Figure 6.3). These results demonstrate that there was much greater retention of copper and lead in the 0-5cm litter layer, than cadmium and zinc. Similar trends have been reported by Martin and co-workers, and are reviewed in Martin and Bullock (1994).

6.5 Sequential Extraction Results: Hallen

The graphs plotted in Figure 6.5 represent the geochemical fractionation results, obtained by sequential extraction, for the metals lead, zinc, cadmium, copper, iron and manganese in a brown earth soil profile from Hallen, site HA. Substantial accumulation of leaf

Figure 6.4 Geochemical Fractionation of Lead and Zinc at Hallen: The graphs illustrate the percentage of lead and zinc in the various geochemical fractions at each depth in the soil profile, determined by sequential extraction. The y-axis is the depth in the soil profile (cm). Each histogram bar is the mean of 6 replicates.

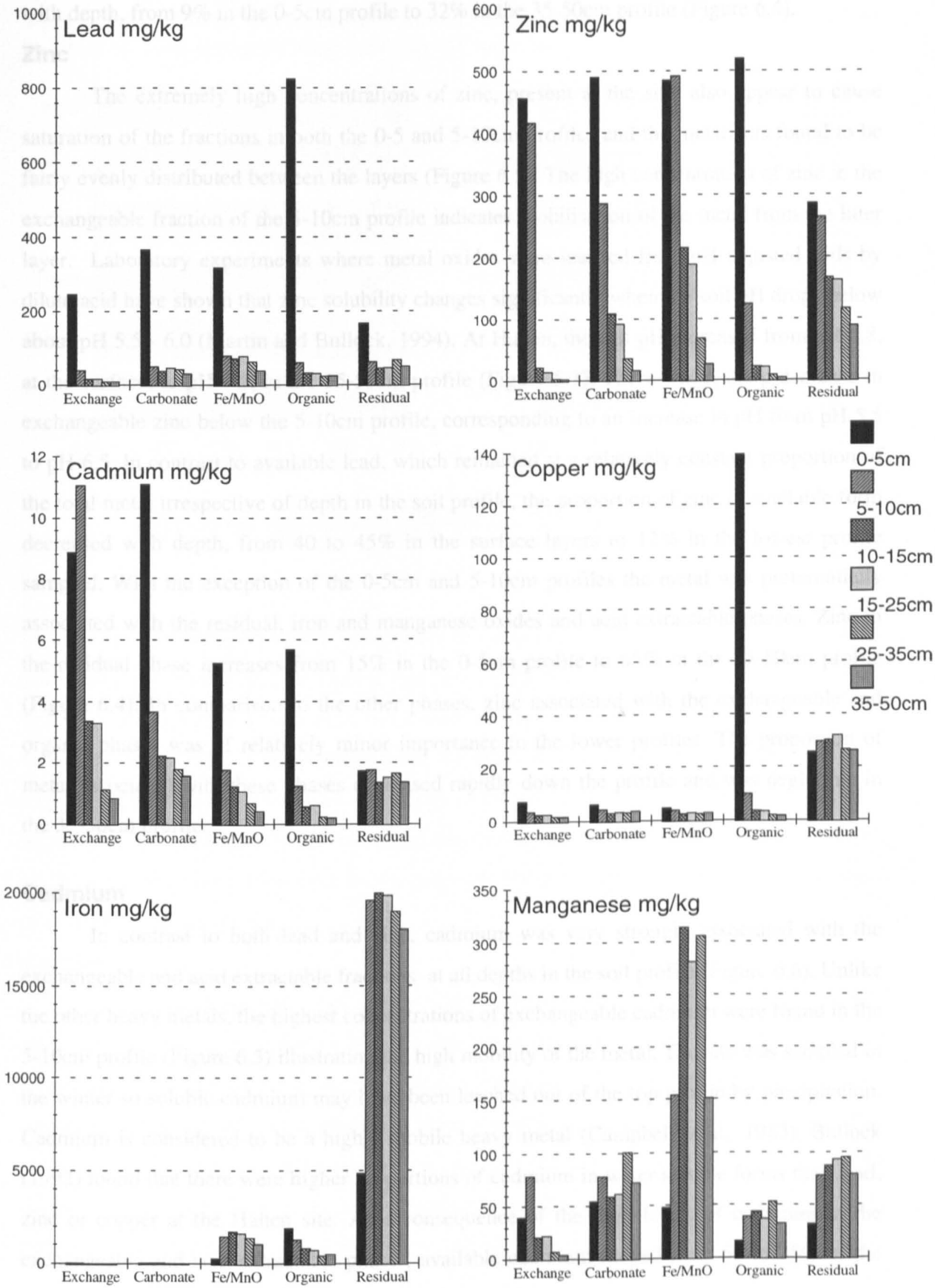


litter containing very high concentrations of heavy metals was observed at the Hallen site. The loss on ignition determination for the 0-5cm litter layer was approximately 70%. Coughtrey et al. (1979) showed that as a result of heavy metal inhibition of decomposition the standing crop of leaf litter at Hallen was nine times greater than at a similar uncontaminated site. The strong associations of lead and copper with the organic phase (Figure 6.5) results in the accumulation of these metals in the litter layer. The 0-5cm profile at Hallen was unique, both in terms of its high organic matter content and the very high concentrations of heavy metal found in the profile. To investigate the processes taking place in the rest of the soil profile the 0-5cm profile was excluded from the statistical analysis.

Lead

In the 0-5cm profile the very high concentration of lead leads to saturation of some of the fractions, resulting in the relatively even distribution of metal between the different soil phases. Below the litter layer, in the mineral soil, lead was strongly associated with the iron and manganese oxides fraction (Figure 6.5). The exchangeable fraction contains the lowest lead concentrations in the mineral soil. The capacity of the exchangeable phase is likely to be considerably lower than the other phases, particularly iron and manganese oxides. Between 25

Figure 6.5 Sequential Extraction of Heavy Metals at Hallen, Site HA: Each graph represents the distribution of a single metal between the five geochemical fractions extracted by the sequential extraction scheme. The histogram bars are plotted in groups of six depicting the metal concentrations (mean 6 replicates) at increasing depth in the soil profile.



and 30% of lead was present in available form. The residual phase increases in importance with depth, from 9% in the 0-5cm profile to 32% in the 35-50cm profile (Figure 6.4).

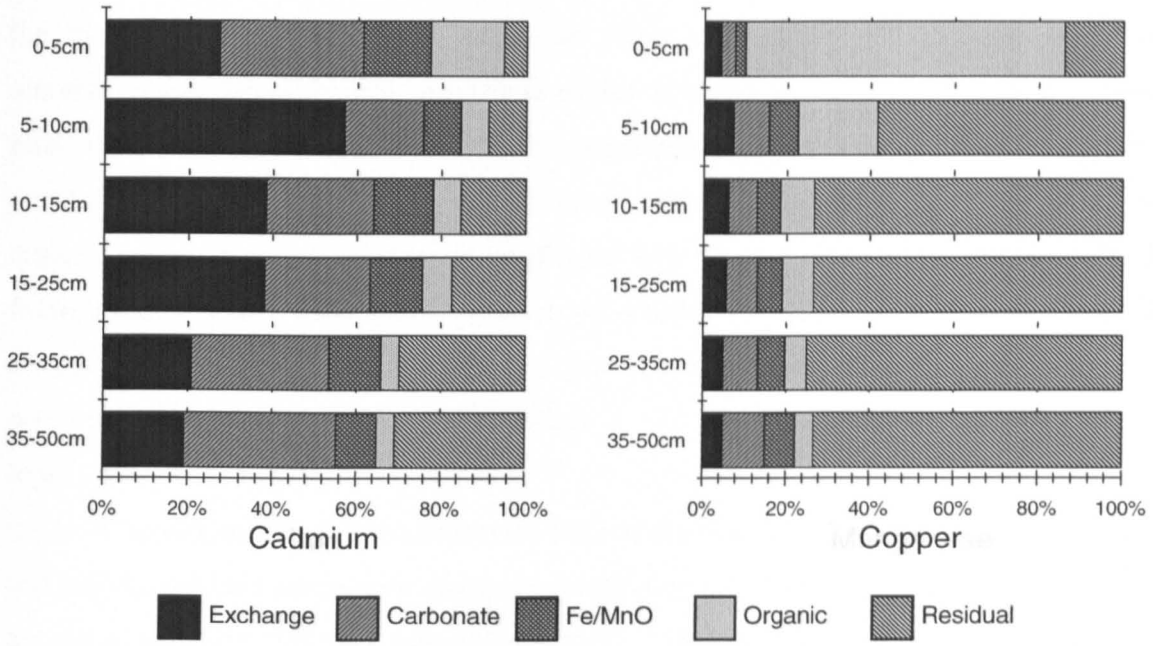
Zinc

The extremely high concentrations of zinc, present at the site, also appear to cause saturation of the fractions in both the 0-5 and 5-10cm profiles and the metal was found to be fairly evenly distributed between the layers (Figure 6.5). The high concentration of zinc in the exchangeable fraction of the 5-10cm profile indicates mobilisation of the metal from the litter layer. Laboratory experiments where metal oxides were leached from pH adjusted soils by dilute acid have shown that zinc solubility changes significantly when the soil pH drops below about pH 5.5 - 6.0 (Martin and Bullock, 1994). At Hallen, the soil pH increased from pH 4.8, at the surface, to pH 7.2, in the 35-50cm profile (Figure 5.1). There was a sharp decrease in exchangeable zinc below the 5-10cm profile, corresponding to an increase in pH from pH 5.5 to pH 6.5. In contrast to available lead, which remained at a relatively constant proportion of the total metal irrespective of depth in the soil profile, the proportion of zinc in available form decreased with depth, from 40 to 45% in the surface layers to 12% in the lowest profile sampled. With the exception of the 0-5cm and 5-10cm profiles the metal was preferentially associated with the residual, iron and manganese oxides and acid extractable phases. Zinc in the residual phase increases from 15% in the 0-5cm profile to 65% in the 35-50cm profile (Figure 6.4). In comparison to the other phases, zinc associated with the exchangeable and organic phases was of relatively minor importance in the lower profiles. The proportion of metal associated with these phases decreased rapidly down the profile and was negligible in the 35-50cm profile.

Cadmium

In contrast to both lead and zinc, cadmium was very strongly associated with the exchangeable and acid extractable fractions at all depths in the soil profile (Figure 6.6). Unlike the other heavy metals, the highest concentrations of exchangeable cadmium were found in the 5-10cm profile (Figure 6.5) illustrating the high mobility of the metal. The site was sampled in the winter so soluble cadmium may have been leached out of the top profile by precipitation. Cadmium is considered to be a highly mobile heavy metal (Campbell et al., 1983). Bullock (1992) found that there were higher proportions of cadmium in water soluble forms than lead, zinc or copper at the Hallen site. As a consequence of the high levels of cadmium in the exchangeable and acid extractable phases, available cadmium ranged from 50 to 75% of the

Figure 6.6 Geochemical Fractionation of Cadmium and Copper at Hallen: The graphs illustrate the percentage of cadmium and copper in the various geochemical fractions at each depth in the soil profile, determined by sequential extraction. The y-axis is the depth in the soil profile (cm). Each histogram bar is the mean of 6 replicates.

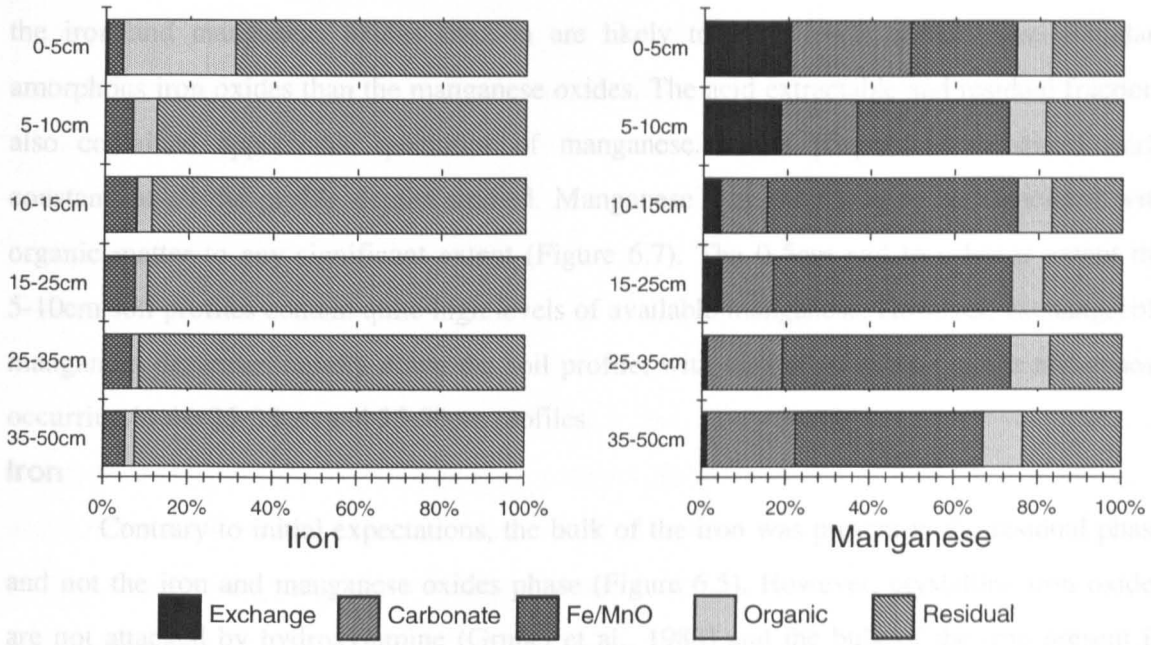


total metal. The relatively low concentration of cadmium in the iron and manganese phase maintained approximately the same proportion of the total metal at all depths in the soil profile. The proportion of cadmium associated with the residual phase increases with depth, from less than 10% in the surface layer to over 30% at 35-50cm. The proportion of exchangeable cadmium decreased with depth in the soil profile, in response to increasingly alkaline soil pH. Scokart et al. (1983) found that cadmium became mobile at a pH of around 6 or less. The small proportion of cadmium associated with the organic matter phase decreased with depth in the soil profile.

Copper

Unlike cadmium and zinc, copper was almost entirely associated with the organic phase in the litter layer (Figure 6.5). The proportion of copper associated with the organic phase decreased with depth in the soil profile (Figure 6.6). Copper was strongly associated with the residual phase at all depths in the mineral soil. In contrast to the results of most other studies, e.g. Griffin et al. (1989), copper was not found to show a strong association with the organic fraction, apart from in the organic surface layer. The availability of copper was almost certainly low, given the small proportions of the metal in the exchangeable and acid

Figure 6.7 Geochemical Fractionation of Iron and Manganese at Hallen: The graphs illustrate the percentage of iron and manganese in the various geochemical fractions at each depth in the soil profile, determined by sequential extraction. The y-axis is the depth in the soil profile (cm). Each histogram bar is the mean of 6 replicates.



extractable phases. Copper was fairly evenly distributed, at low concentrations, between the exchangeable, acid extractable, iron and manganese oxides and organic matter phases.

There were essentially two processes controlling the speciation of copper at Hallen. Aerial deposition was trapped by the surface organic layer with little evidence for mobilisation of copper into the mineral soil. The copper concentrations in the mineral soil are essentially the natural background levels of the element, which is an important micronutrient. The proportion of copper associated with the organic matter phase (Figure 6.6) was less than expected at all depths in the soil profile except the 0-5cm, litter layer. One reason for the unusual behaviour of copper could be the presence of far higher concentrations of lead and zinc competing for binding sites on organic matter. Although copper has a higher affinity for organic matter binding sites, competition between metals at such different concentrations may favour the much more abundant metals, lead and zinc, over copper which was present at much lower concentrations.

Manganese

As well as being present as an oxide in the soil, manganese may occur in other forms such as exchangeable cations or complexed with organic matter. The graph of manganese fractionation at different depths in the soil profile (Figure 6.5) shows that the highest

concentrations occurred in the iron and manganese oxides fraction, confirming the selectivity of the hydroxylamine extraction. These results also indicate that the concentration of manganese in the soil was lower than iron. As a consequence, the metal binding properties of the iron and manganese oxides fraction are likely to be a result of the more abundant amorphous iron oxides than the manganese oxides. The acid extractable and residual fractions also contained appreciable quantities of manganese. These proportions remained fairly constant, at all the profile depths studied. Manganese was not found to be associated with organic matter to any significant extent (Figure 6.7). The 0-5cm and to a lesser extent the 5-10cm soil profiles contain quite high levels of available manganese. However, exchangeable manganese decreases rapidly down the soil profile, with almost no exchangeable manganese occurring in the 25-35cm and 35-50cm profiles.

Iron

Contrary to initial expectations, the bulk of the iron was present in the residual phase and not the iron and manganese oxides phase (Figure 6.5). However, crystalline iron oxides are not attacked by hydroxylamine (Grubel et al., 1988) and the bulk of the iron present in most soils is probably in the form of crystalline iron oxides. Heavy metals inside the crystal lattice of crystalline iron oxides are therefore very unlikely to become available, or be transferred to other fractions. It is the heavy metals associated with the amorphous iron oxides that are important in the study of heavy metal speciation in soils. Although detectable levels of iron were found in the exchangeable and acid extractable fractions, they were insignificant as a proportion of the total iron present in the soil. A significant proportion of the iron was found to be associated with the organic matter phase in the upper two profiles (Figure 6.7). Amorphous iron oxides often occur in combination with humic substances forming multi-layered coatings on mineral particles (Schnitzer, 1969).

6.6 Geochemical Fractionation and Soil Properties, Site HA

Regression analysis was used to investigate the relationships between the geochemical fractionation of heavy metals and the soil properties at different depths in the soil profile. In Chapter 5 (Table 5.4) correlation of the soil properties at Hallen showed high associations between all four soil properties measured: pH, cation exchange complexation, organic carbon and pyrophosphate extractable iron. In view of this, regression analysis was used to investigate the relationship between a specific fraction and a single soil property. The coefficients depend on the concentration of the metal in the fraction, as the soil scale for the soil property was the

same for each metal studied. Hence, lead and zinc, which were found at the site at far higher concentrations than copper and cadmium, tend to have higher coefficients. There was a noticeable discontinuity between the 0-5cm profile and the mineral soil, both in terms of the far higher concentrations of lead and copper and the much greater proportion of organic carbon. In view of this, the litter layer was excluded from the statistical analysis at Hallen allowing relationships in the mineral soil to be examined. In the case of zinc both the 0-5cm and 5-10cm profiles were excluded, due to the very high concentrations of zinc in these layers compared to the remainder of the soil (Figure 6.5).

Metals in the Exchangeable Phase

The metals released in the exchangeable fraction were associated with cation exchange sites and should therefore be directly related to the cation exchange capacity of the soil. However, the exchangeable fraction also contains metals from the soil solution which may obscure the relationship. As anticipated, a high proportion of the variance in exchangeable metal concentrations was attributable to cation exchange capacity (Table 6.1).

Table 6.1 Exchangeable Fraction and Cation Exchange Capacity

Model: Exchangeable HM = CONSTANT + CEC N=28

Exchangeable HM - heavy metals extracted in the exchangeable fraction.

Metal	Soil Property Included in the subset model	Adjusted Squared Multiple R	Coefficient 'slope'	P (2 Tail) T-test
Lead	CEC	82.3	1.19	0.000
Zinc (1)	CEC	93.1	1.21	0.000
Cadmium	CEC	80.4	0.387	0.000
Copper	CEC	80.1	0.078	0.000

(1) 0-5cm and 5-10cm profiles excluded, N=22.

Organic matter was also considered as an important source of cation exchange capacity. As exchange processes are important in the litter layer, the regression model was calculated using all the soil profiles. Ninety nine percent of the variation in exchangeable lead was explained by soil organic carbon content (Table 6.2). The strong association of exchangeable lead with organic carbon suggests that a significant fraction of the metal was weakly bound to organic matter, similar observations were made, by Griffin et al. (1989). A high proportion of the variance in exchangeable copper was also accounted for by organic carbon. Exchangeable zinc and cadmium were not strongly related to organic carbon content.

Table 6.2 Exchangeable Fraction and Organic Carbon

Model: Exchangeable HM = CONSTANT + OC N=34

Exchangeable HM - heavy metals extracted in the exchangeable fraction.

Metal	Soil Property Included in the subset model	Adjusted Squared Multiple R	Coefficient 'slope'	P (2 Tail) T-test
Lead	OC	99.2	7.05	0.000
Zinc	OC	50.6	11.9	0.000
Cadmium	OC	27.2	0.173	0.001
Copper	OC	91	0.159	0.000

Similar results were obtained in a study of lead, zinc, cadmium and copper in cation, anionic, neutral and low molecular weight polar organic forms, by Bullock (1992), in the soil solution at Hallen wood. Low polar organic forms were found to be most important for lead and copper, cadmium and zinc were mainly present in cationic forms.

Iron and Manganese Oxides Fraction

Heavy metal associations with the iron and manganese oxides fraction were examined in relation to the amorphous iron content of the soil (Table 6.3). There were weak but significant associations between lead and copper in the iron and manganese oxides fraction and pyrophosphate extractable iron. Cadmium and zinc concentrations in the iron and manganese oxides phase were strongly related to amorphous iron. The review of studies of the geochemical fractionation of cadmium and zinc in Chapter 2 (Table 2.5) demonstrated that these metals were usually strongly associated with the iron and manganese oxides fraction.

Table 6.3 Iron and Manganese Oxides Fraction and Soil Properties

Model: FeMnO HM = CONSTANT + pH + PyrFe n=30

FeMnO HM - heavy metals extracted in the iron and manganese oxides fraction.

PyrFe - Pyrophosphate extractable iron.

Metal	Soil Properties Included in the subset model	Adjusted Squared Multiple R	Coefficient 'slope'	P (2 Tail) T-test
Lead	PyrFe	38.9	0.024	0.000
Zinc (1)	PyrFe	87.4	0.33	0.000
Cadmium	PyrFe	89.7	0.001	0.000
Copper	PyrFe	50.7	0.001	0.000

(1) 0-5cm and 5-10cm profiles excluded, N=24.

Organic Matter Fraction

The heavy metal concentrations in the organic matter fraction of the sequential extraction scheme were regressed against soil organic carbon concentrations. Significant, but not very large, proportions of the variances of all four heavy metals were described by organic carbon content (Table 6.4). Heavy metals may become associated with organic matter by a number of different mechanisms. The comparisons of heavy metal concentrations in the organic fraction with estimates of organic carbon content were not sufficiently specific to yield useful results. Organic matter interactions with heavy metals at Hallen are described in more detail in Chapter 7.

Table 6.4: Organic Matter Fraction and Soil Properties

Model: Organic HM = CONSTANT + OC n=30

Organic HM - heavy metals extracted in the organic fraction.

Metal	Soil Properties Included in the subset model	Adjusted Squared Multiple R	Coefficient 'slope'	P (2 Tail) T-test
Lead	OC	65.1	7.33	0.000
Zinc (1)	OC	84.1	5.932	0.000
Cadmium	OC	76.6	0.228	0.000
Copper	OC	63.8	1.62	0.000

(1) 0-5cm and 5-10cm profiles excluded, N=24.

6.7 Heavy Metal Distribution in the Soil Profile at Hallen

The very high concentrations of lead, zinc, cadmium and copper in the surface layers of the brown earth soil profile at Hallen wood have resulted in a very deep layer of organic matter from litter fall, due to the inhibition of organic matter decomposition (Coughtrey et al., 1979). The results suggest that a large proportion of the aerial deposition of heavy metals from the industrial complex was immobilised in the organic matter layer. Nitric and sulphuric acid deposition at the site, from the industrial complex at Avonmouth, results in the mobilisation of cadmium and zinc from the surface layers, while lead and copper appear to be immobilised by the organic layer. These results demonstrate the differences in the heavy metal affinities for organic matter and the different susceptibilities of these metals to mobilisation by acid deposition, observed in other studies (e.g. Scokart et al., 1983; Griffin et al., 1989).

6.8 Geochemical Fractionation of Heavy Metals At Ringinglow

At Ringinglow, the highest concentrations of lead were around 250mg/kg in the RG and RB soil profiles and 650mg/kg in the SRG soil profile, a factor of 5 to 10 lower than at Hallen. The different lead concentrations found at the three Ringinglow sites reflect the position of the sampling site relative to the smelter. Unlike sites RG and RB, site SRG lies downwind of the smelter and would have received higher rates of aerial deposition. The metal inputs to the Ringinglow site are discussed in Chapter 4. Smelting at Ringinglow took place in the 19th Century, whereas the smelting at Avonmouth has taken place over the last 60 years. The decrease in total lead concentrations down the soil profile at sites RG and RB was much more gradual than at Hallen, reflecting the fact that the lead has been in the soil much longer, so there had been more time for metal transport down the soil profile. Unlike the sample from Hallen, there was sufficient nickel in the soil samples from the Ringinglow site to allow the determination of nickel in the sequential extraction extracts.

Three factors control the distribution of heavy metals in the soil profile:

(i) Aerial deposition,

(ii) Weathering of the substrate,

(ii) Soil/plant circulation.

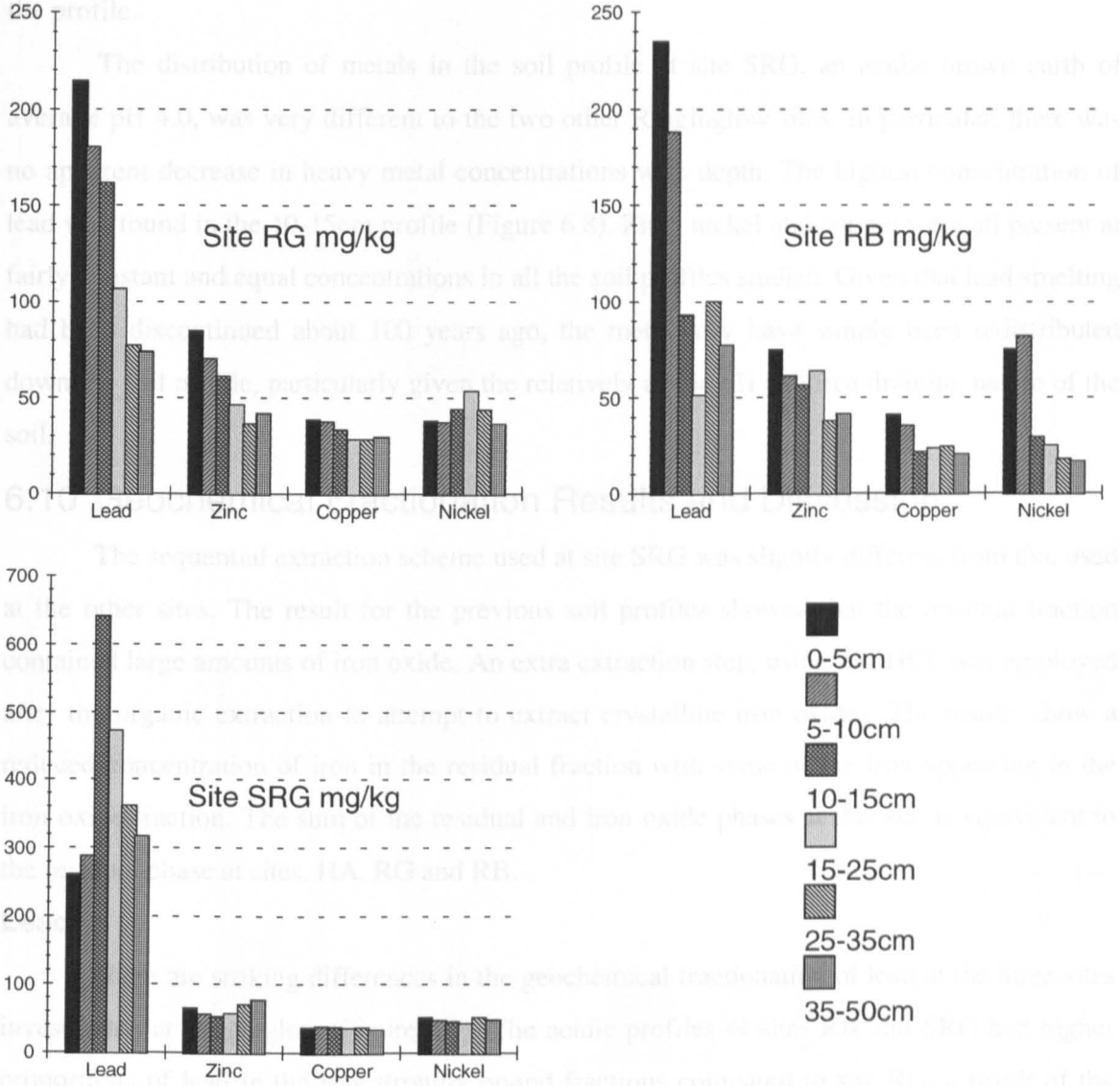
Heavy metals enter the soil from a variety of inputs including, impurities in the ore smelted, steel works and other industrial activity in Sheffield.

The close proximity of the three sites at Ringinglow means that differences in the geochemical fractionation of heavy metals between these sites are attributable to differences in the soil characteristic, as the sites share similar heavy metal inputs and climatic conditions. The geochemical fractionation of each metal in the three different soil types is discussed in relation to the chemical properties and composition of the soil profiles at the three sites, with particular reference to pH.

6.9 Total Heavy Metal Concentrations at Ringinglow

Lead concentrations at site RG, a neutral stagnogley, decreased down the soil profile, so that in the 35-50cm profile the concentration of lead was 35% of that in the 0-5cm profile (Figure 6.8). The total zinc concentration also decreased down the profile, more gradually than lead, the zinc concentration in the 35-50cm profile was found to be half that at the top layer of the soil profile. Total copper concentration in the soil was found to decrease slightly

Figure 6.8 Total Digestion of Heavy Metals at Ringinglow: Each graph represents the total metal concentrations at a site, which are plotted in mg/kg on the y-axis. These determinations were made by hot nitric acid digestion. The histogram bars are plotted in groups of six depicting the metal concentrations (mean 6 replicates) at increasing depth in the soil profile.



with depth in the soil profile. Unlike lead and zinc, total nickel concentrations did not vary with depth in the soil profile in the profiles sampled.

The concentrations of the heavy metals lead, zinc, copper and nickel decreased with depth in the acidic podzol at site RB (Figure 6.8). However, unlike the results at site RG, the concentrations of lead in the 25-35cm and 35-50cm profiles were higher than the concentrations in the 10-15cm and 15-25cm profiles indicating possible organic matter accumulation of metals below 25cm in the soil profile. The graph of organic carbon concentration in Chapter 5 (Figure 5.4) showed an increase in organic carbon in the 15-25cm, 25-35cm, and 35-50cm soil profiles. The concentrations of zinc in the soil profiles were found to be at fairly similar levels in the first 25cm of the soil and lower below 25cm. Nickel

concentration in the top 10cm of the soil was three times greater than those at lower depths in the profile.

The distribution of metals in the soil profile at site SRG, an acidic brown earth of average pH 4.0, was very different to the two other Ringinglow sites. In particular, there was no apparent decrease in heavy metal concentrations with depth. The highest concentration of lead was found in the 10-15cm profile (Figure 6.8). Zinc, nickel and copper were all present at fairly constant and equal concentrations in all the soil profiles studied. Given that lead smelting had been discontinued about 100 years ago, the metal may have simply been redistributed down the soil profile, particularly given the relatively acidic pH and free draining nature of the soil.

6.10 Geochemical Fractionation Results and Discussion

The sequential extraction scheme used at site SRG was slightly different from that used at the other sites. The result for the previous soil profiles showed that the residual fraction contained large amounts of iron oxide. An extra extraction step, using 2M HCl, was employed after the organic extraction to attempt to extract crystalline iron oxides. The results show a reduced concentration of iron in the residual fraction with some of the iron appearing in the iron oxide fraction. The sum of the residual and iron oxide phases at this site is equivalent to the residual phase at sites, HA, RG and RB.

Lead

There are striking differences in the geochemical fractionation of lead at the three sites investigated at Ringinglow (Figure 6.9). The acidic profiles of sites RB and SRG had higher proportions of lead in the less strongly bound fractions compared to site RG, a result of the lower pH, pH 4 compared to pH 6, at these sites.

The geochemical fractionation of lead in the neutral stagnogley, site RG, changed substantially with increasing depth in the soil profile. The highest proportion of lead was found in the residual fraction at all depths in the soil profile. Lead associated with the iron and manganese oxides and organic matter phases decreased with depth, both as an absolute concentration (Figure 6.9) and as a proportion of total lead (Figure 6.10). In contrast, the concentration of lead in the exchangeable and acid extractable bound forms remains relatively constant down the soil profile. As a result the proportion of lead in the exchangeable and acid extractable fractions became significantly more important with increasing depth in the soil profile (Figure 6.10). The net result was that in the surface layers of the soil the bulk of the

Figure 6.9 Sequential Extraction of Lead and Zinc at Ringinglow, Sites RG, RB and SRG: Each graph represents the distribution of a single metal between the geochemical fractions determined by sequential extraction. The histogram bars are plotted in groups of six depicting the concentrations (mean 6 replicates) at increasing depth in the soil profile.

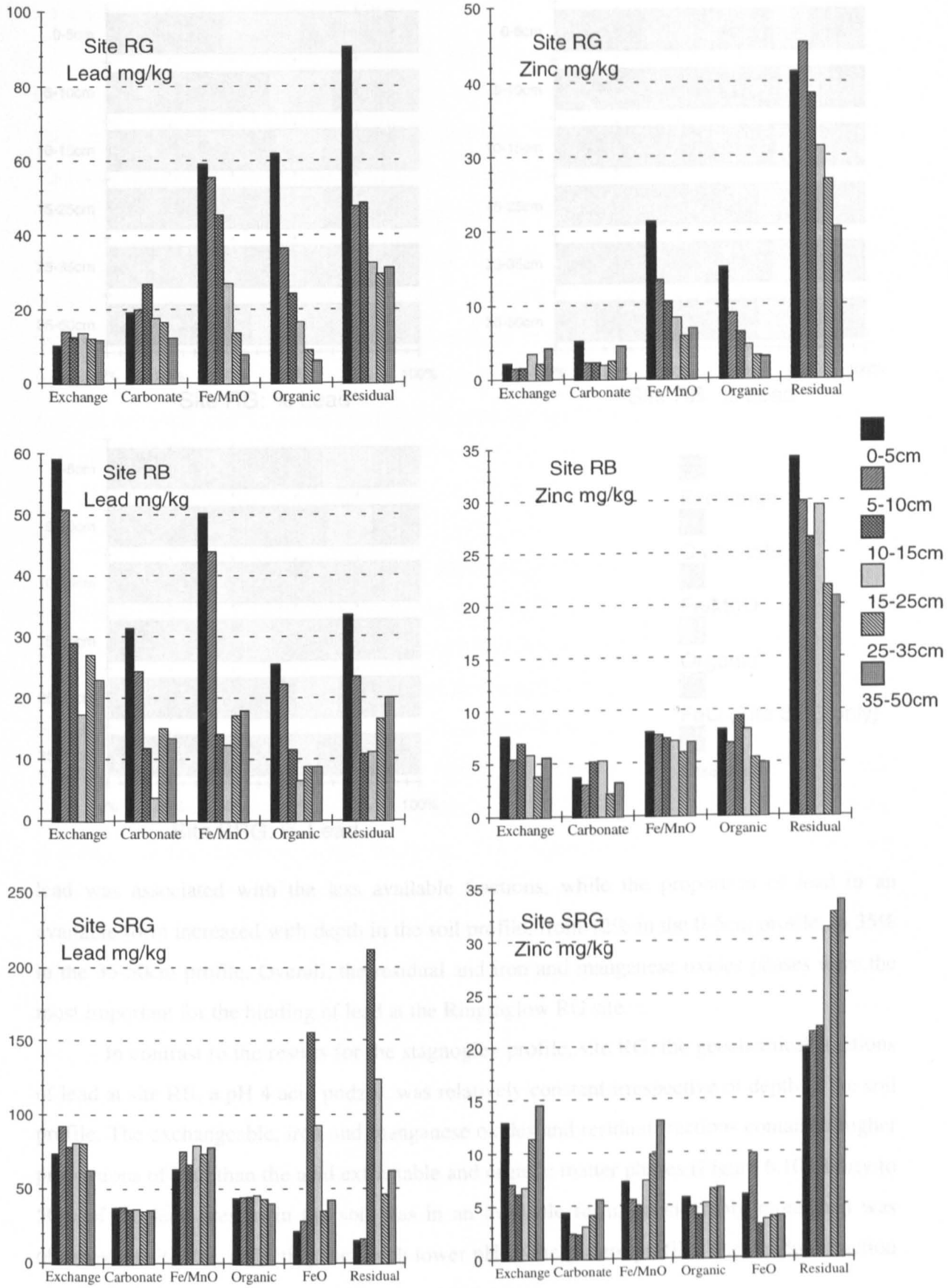
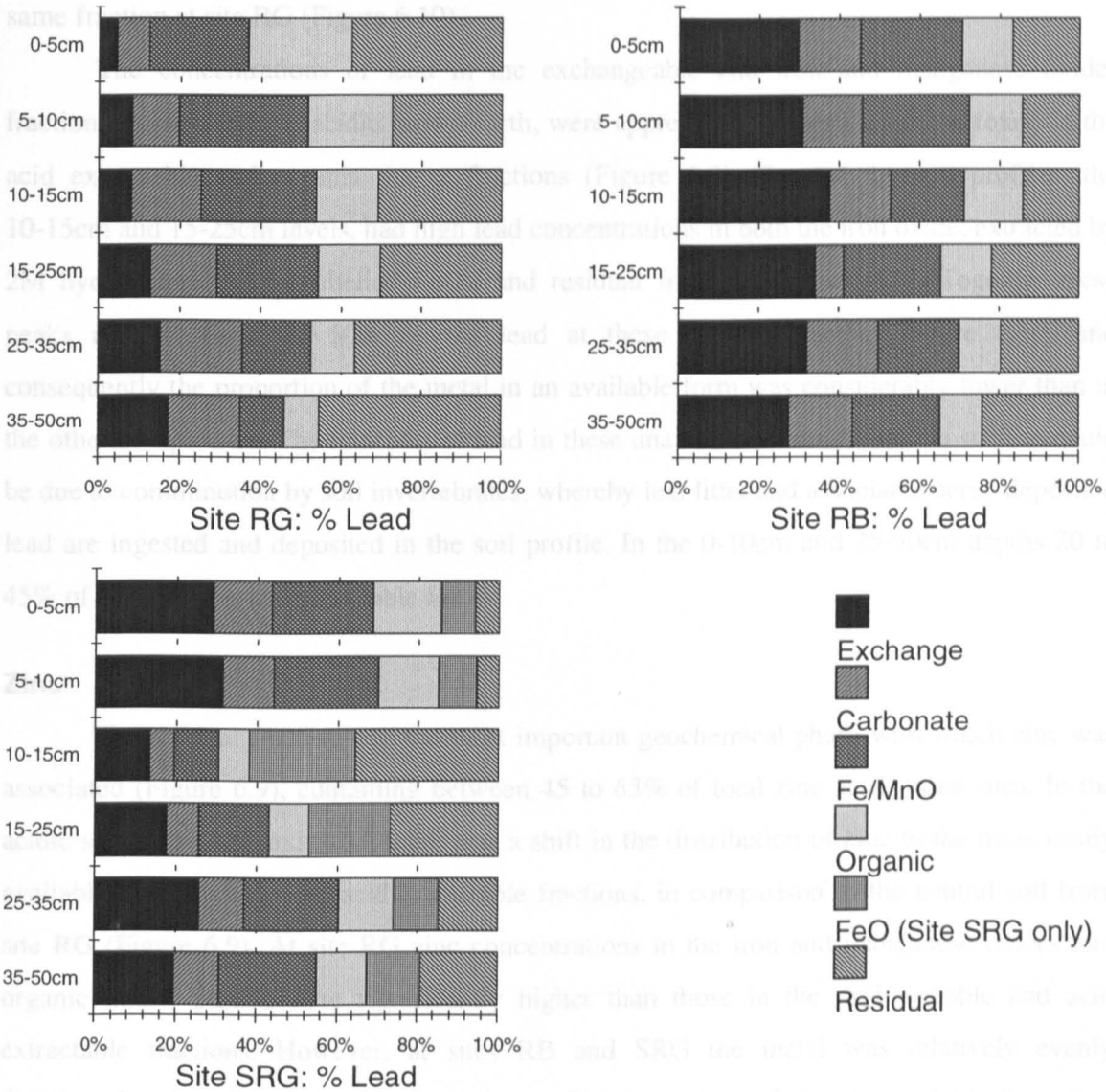


Figure 6.10 Geochemical Fractionation of Lead at Ringinglow: Each graph illustrates the percentage of lead in the various geochemical fractions at each depth in the soil profile, determined by sequential extraction. The y-axis is the depth in the soil profile (cm). The FeO fraction is a 2M HCl extraction for crystalline iron and was used at site SRG only.



lead was associated with the less available fractions, while the proportion of lead in an available form increased with depth in the soil profile, from 12% in the 0-5cm profile, to 35% in the 35-50cm profile. Overall, the residual and iron and manganese oxides phases were the most important for the binding of lead at the Ringinglow RG site.

In contrast to the results for the stagnogley profile, site RG, the geochemical fractions of lead at site RB, a pH 4 acid podzol, was relatively constant irrespective of depth in the soil profile. The exchangeable, iron and manganese oxides and residual fractions contained higher proportions of lead than the acid extractable and organic matter phases (Figure 6.10). Forty to 50% of the lead present in the soil was in an available form, considerably more than was observed at site RG, reflecting the much lower pH of the podzol profile. The residual fraction

was associated with about 14 to 22% of total lead, much less than the proportion found in the same fraction at site RG (Figure 6.10).

The concentrations of lead in the exchangeable and iron and manganese oxides fractions at site SRG, an acidic brown earth, were appreciably higher than those found in the acid extractable and organic matter fractions (Figure 6.9). Two of the soil profiles, the 10-15cm and 15-25cm levels, had high lead concentrations in both the iron oxide, extracted by 2M hydrochloric acid (Labelled FeO), and residual fractions (Figure 6.9). Together these peaks account for over 50% of the lead at these profiles depths (Figure 6.10) and consequently the proportion of the metal in an available form was considerably lower than in the other soil profiles. The transport of lead in these unavailable forms from the surface could be due to comminution by soil invertebrates, whereby leaf litter and associated aerial deposited lead are ingested and deposited in the soil profile. In the 0-10cm and 25-50cm depths 20 to 45% of the lead was in an available form.

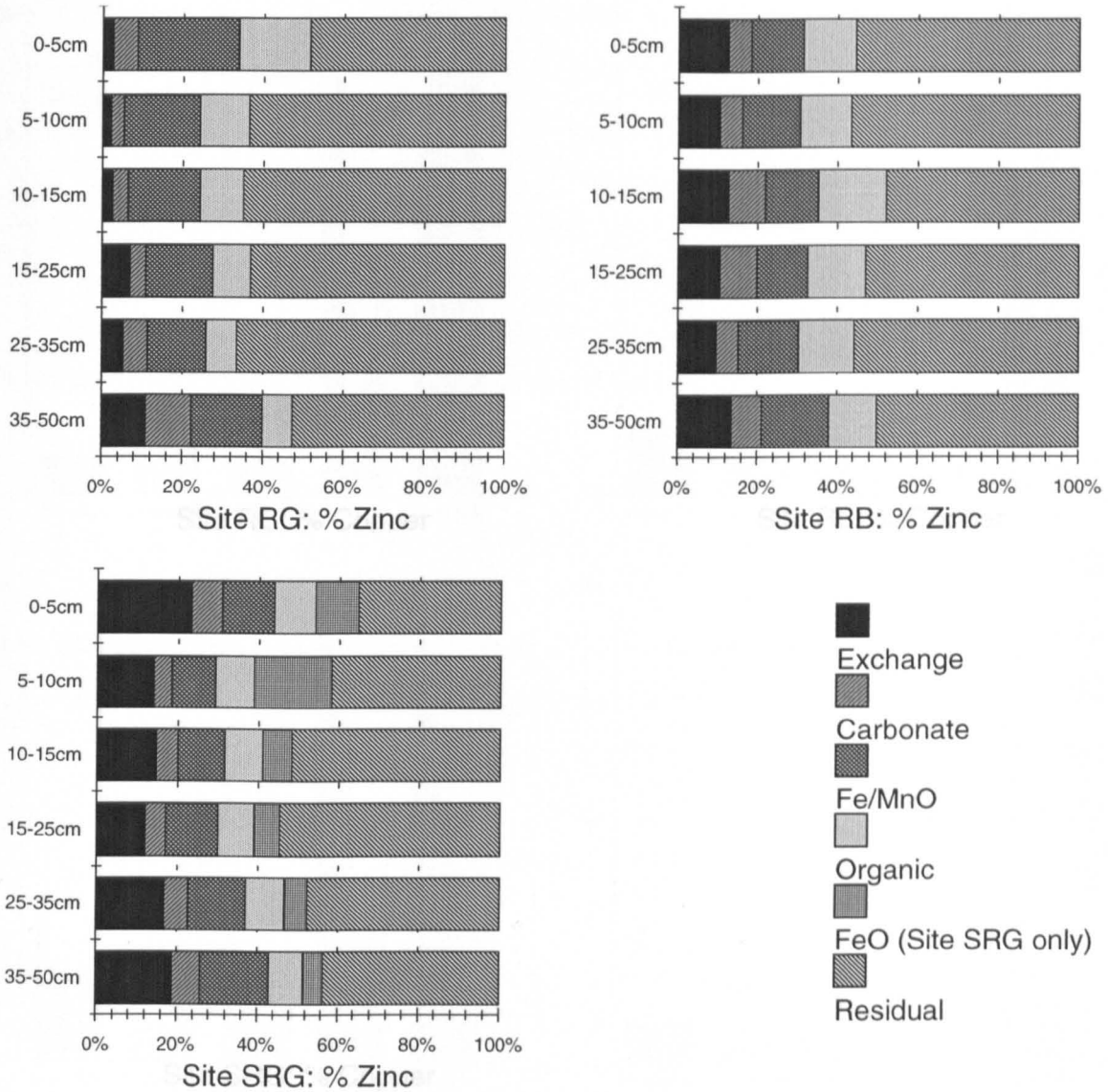
Zinc

The residual fraction was the most important geochemical phase with which zinc was associated (Figure 6.9), containing between 45 to 65% of total zinc at all three sites. In the acidic soils, sites RB and SRG, there was a shift in the distribution of zinc to the more easily available exchangeable and acid extractable fractions, in comparison to the neutral soil from site RG (Figure 6.9). At site RG zinc concentrations in the iron and manganese oxides and organic matter phases were significantly higher than those in the exchangeable and acid extractable fractions. However, at sites RB and SRG the metal was relatively evenly distributed among the non-residual fractions. The proportion of zinc in available form was considerably less than that of lead at all depths in the soil profile.

Like lead, zinc associated with the iron and manganese oxides and organic matter fractions at site RG decreased with depth in the soil profile, both as absolute concentrations and as a proportion of the total concentrations of the metal. The percentage of zinc in an available form increased with depth in the soil profile (Figure 6.11), from 12% in the 0-5cm profile to 22% in the 35-50cm profile. However, the bulk of the metal occurred in less available fractions, particularly the residual fraction.

At site RB the exchangeable, iron and manganese oxides and organic phases contained slightly higher concentrations of zinc than the acid extractable phase (Figure 6.9). The residual bound fraction accounts for 50 to 55% of the total zinc (Figure 6.11). Available zinc

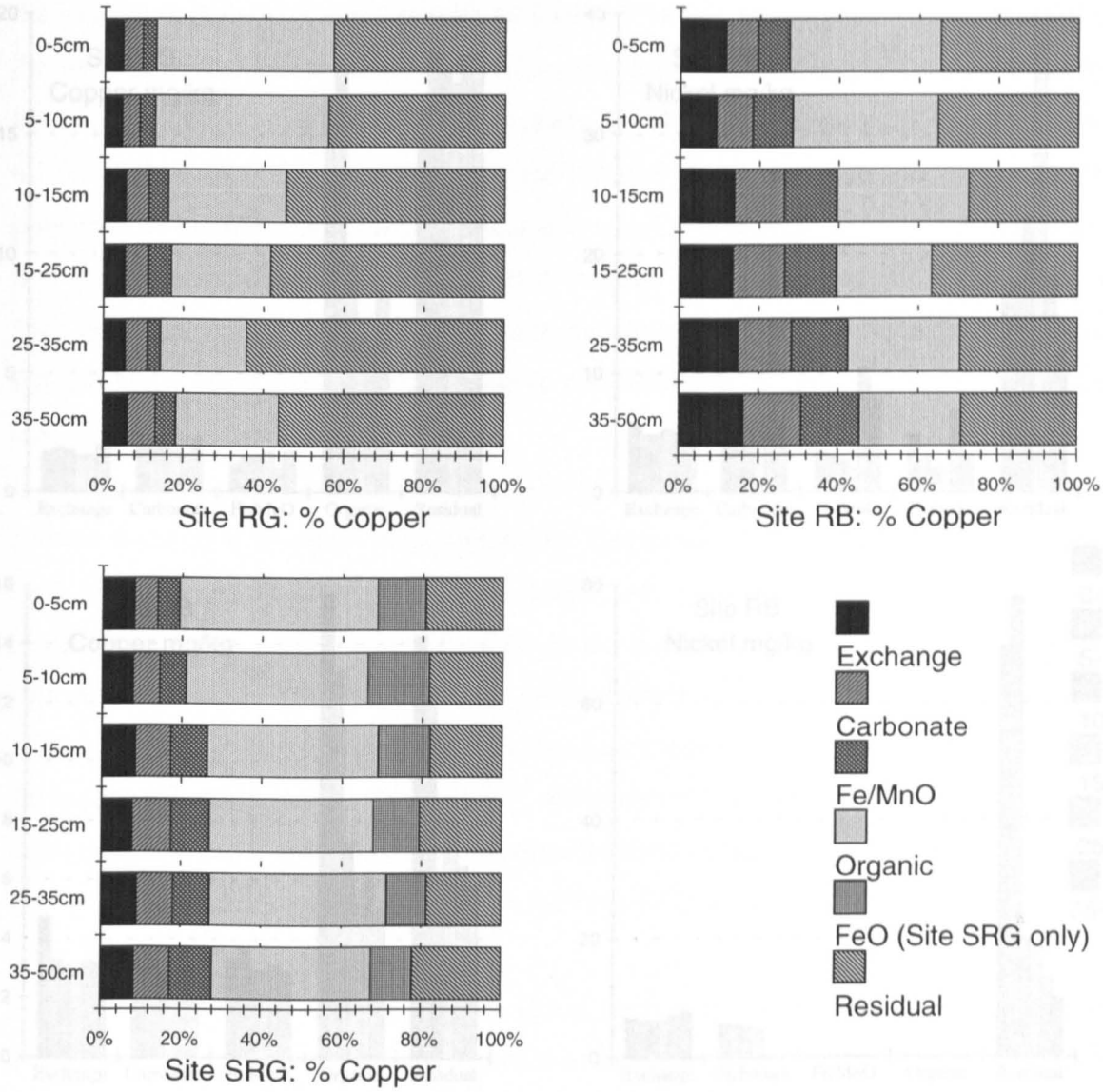
Figure 6.11 Geochemical Fractionation of Zinc at Ringinglow: Each graph illustrates the percentage of zinc in the various geochemical fractions at each depth in the soil profile, determined by sequential extraction. The y-axis is the depth in the soil profile (cm). The FeO fraction was a 2M HCl extraction for crystalline iron carried out at site SRG only.



fluctuated between 15 and 22%, which was significantly higher than at the RG site, with the exception of the 35-50cm profile. The acid extractable, iron and manganese oxides and organic phases were associated with relatively constant proportions of the total metal at all depths in the soil profile.

Like lead, zinc concentrations at site SRG were lower in the acid extractable and organic matter phases (Figure 6.9). The iron oxide fraction (Labelled FeO), extracted by 2M hydrochloric acid also contained low concentrations of zinc. Forty five to 61% of zinc was found in the residual and iron oxide fractions (Figure 6.11). The proportion of zinc in available form was highest at the top of the soil profile at 31%, reached a minimum of 17% at 15-25cm and then increased to 26% in the 35-50cm profile.

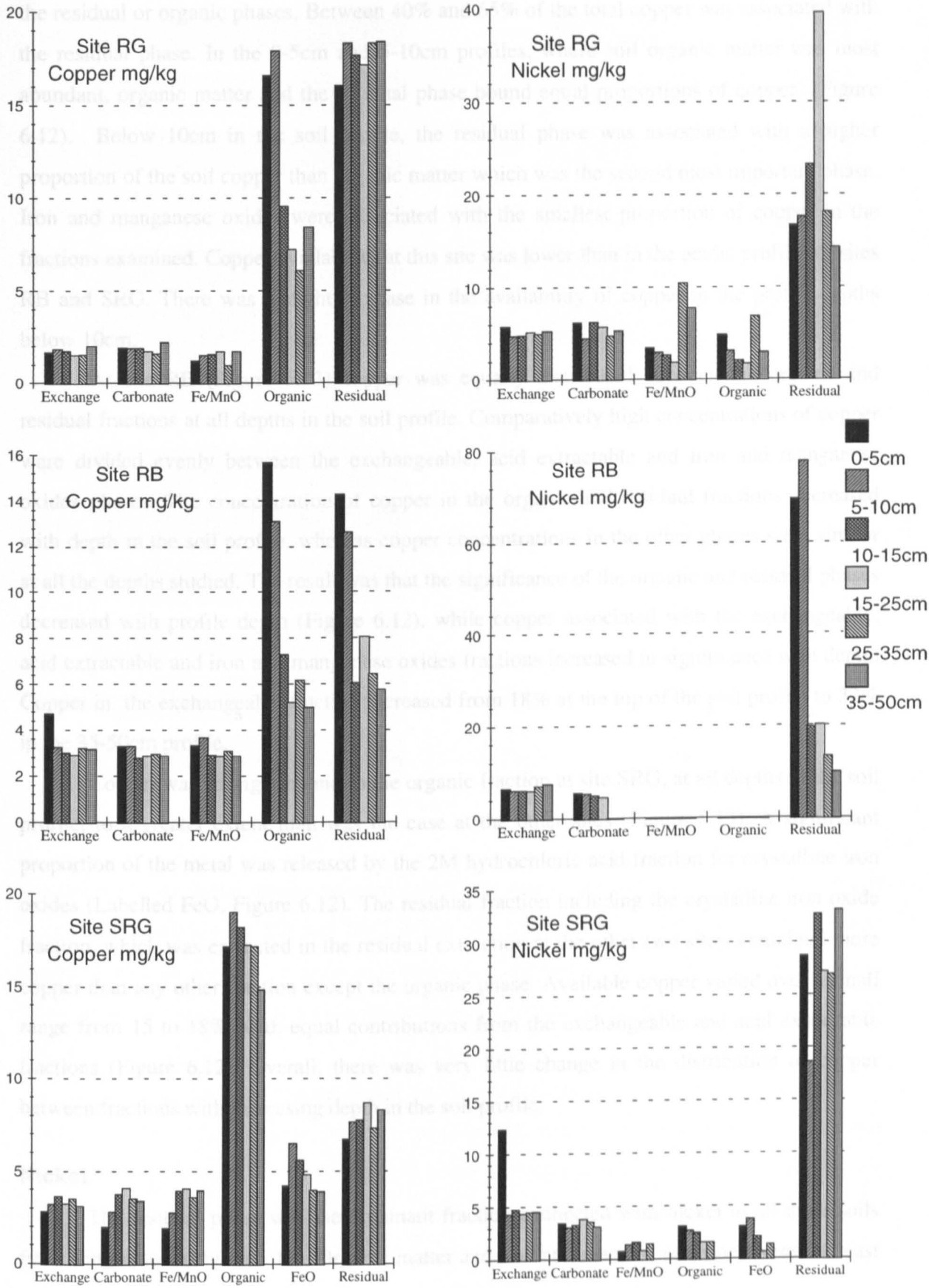
Figure 6.12 Geochemical Fractionation of Copper at Ringinglow: Each graph illustrates the percentage of copper in the various geochemical fractions at each depth in the soil profile, determined by sequential extraction. The y-axis is the depth in the soil profile (cm). The FeO fraction is a 2M HCl extraction for crystalline iron and was used at site SRG only.



Copper

The organic matter and residual phases were the main fractions with which copper was associated (Figure 6.13). In the acidic profiles of sites RB and SRG, the residual phase was associated with a significantly lower proportion of total copper than was the case in the neutral soil at site RG. The highest proportion of copper in an available form was found in the acid podzol from site RB. Low concentrations of copper were evenly distributed between the exchangeable, acid extractable and iron and manganese oxides fractions at all three sites. The strong association of copper with organic matter observed in these Ringinglow soil profiles was similar to that found by other studies of the geochemical fractionation of copper in soils (Hickey and Kittrick, 1984; Ramos et al., 1994).

Figure 6.13 Sequential Extraction of Copper and Nickel at Ringinglow, Sites RG, RB and SRG: Each graph represents the distribution of a single metal between the geochemical fractions determined by sequential extraction. The histogram bars are plotted in groups of six depicting the concentrations (6 replicates) at increasing depth in the soil profile.



At site RG, over 80% of copper at any of the profile depths studied occurred in either the residual or organic phases. Between 40% and 65% of the total copper was associated with the residual phase. In the 0-5cm and 5-10cm profiles, where soil organic matter was most abundant, organic matter and the residual phase bound equal proportions of copper (Figure 6.12). Below 10cm in the soil profile, the residual phase was associated with a higher proportion of the soil copper than organic matter which was the second most important phase. Iron and manganese oxides were associated with the smallest proportion of copper in the fractions examined. Copper availability at this site was lower than in the acidic profiles of sites RB and SRG. There was a slight increase in the availability of copper in the profile depths below 10cm.

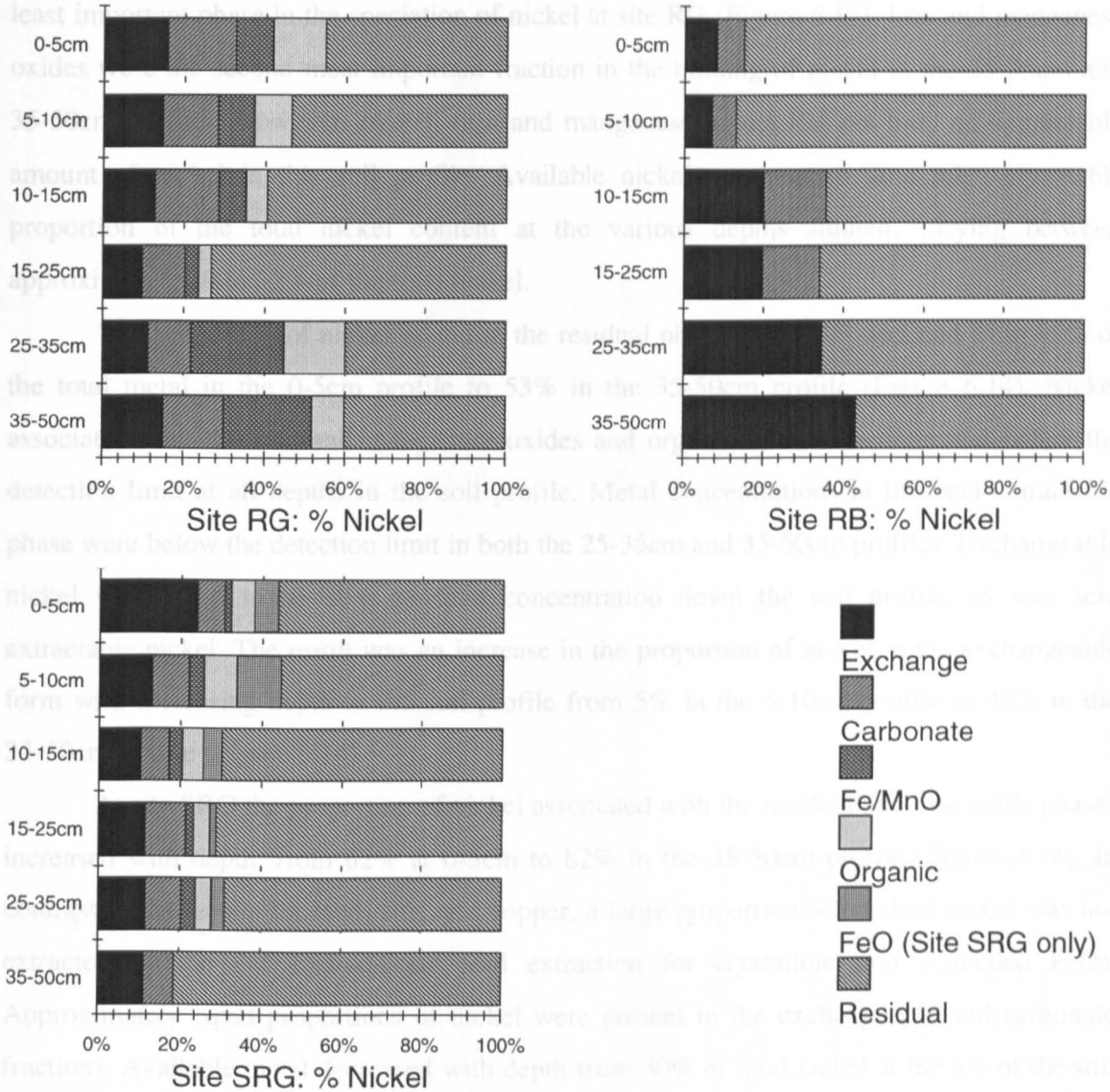
At site RB (Figure 6.13) copper was equally distributed between the organic and residual fractions at all depths in the soil profile. Comparatively high concentrations of copper were divided evenly between the exchangeable, acid extractable and iron and manganese oxides phases. The concentration of copper in the organic and residual fractions decreased with depth in the soil profile, whereas copper concentrations in the other phases were similar at all the depths studied. The result was that the significance of the organic and residual phases decreased with profile depth (Figure 6.12), while copper associated with the exchangeable, acid extractable and iron and manganese oxides fractions increased in significance with depth. Copper in the exchangeable fraction increased from 18% at the top of the soil profile to 32% in the 35-50cm profile.

Copper was strongly bound to the organic fraction at site SRG, at all depths in the soil profile, to a greater extent than was the case at the other sites (Figure 6.13). A significant proportion of the metal was released by the 2M hydrochloric acid fraction for crystalline iron oxides (Labelled FeO, Figure 6.12). The residual fraction including the crystalline iron oxide fraction, which was extracted in the residual extraction at the other two sites, contained more copper than any other fraction except the organic phase. Available copper varied over a small range from 15 to 18%, with equal contributions from the exchangeable and acid extractable fractions (Figure 6.12). Overall, there was very little change in the distribution of copper between fractions with increasing depth in the soil profile.

Nickel

The residual phase was the dominant fraction connected with nickel in all three soils from Ringinglow (Figure 6.13). Organic matter and iron and manganese oxides were the least

Figure 6.14 Geochemical Fractionation of Nickel at Ringinglow: Each graph illustrates the percentage of nickel in the various geochemical fractions at each depth in the soil profile, determined by sequential extraction. The y-axis is the depth in the soil profile (cm). The FeO fraction is a 2M HCl extraction for crystalline iron and was used at site SRG only.



important phases in the speciation of nickel. There was a significant difference between the acidic soil profiles, sites RB and SRG, where the iron and manganese oxides and organic matter phases were of minor or no importance and the neutral soil profile of site RG where these phases were associated with a much larger proportion of the total nickel content of the soil (Figure 6.14)

Like lead, zinc and copper, nickel was strongly associated with the residual fraction at site RG (Figure 6.13). However, there was considerable variation in the proportion of nickel in the residual phase, in the 25-35cm and 35-50cm profiles the residual fraction accounted for 40% of the total nickel metal, compared to 70% in the 15-25cm profile (Figure 6.14). Nickel was found to be at slightly higher concentrations in the exchangeable and acid extractable

fractions than in the iron and manganese and organic fractions. Overall, organic matter was the least important phase in the speciation of nickel at site RG (Figure 6.14). Iron and manganese oxides were the second most important fraction in the binding of nickel in the 25-35cm and 35-50cm profiles. However, overall iron and manganese oxides did not bind an appreciable amount of nickel in this soil profile. Available nickel was present at a relatively stable proportion of the total nickel content at the various depths studied, varying between approximately 20 to 32% of the total nickel.

The proportion of nickel bound in the residual phase at site RB declined from 88% of the total metal in the 0-5cm profile to 53% in the 35-50cm profile (Figure 6.14). Nickel associated with the iron and manganese oxides and organic matter fractions was below the detection limit at all depths in the soil profile. Metal concentrations in the acid extractable phase were below the detection limit in both the 25-35cm and 35-50cm profiles. Exchangeable nickel was found to be at a constant concentration down the soil profile, as was acid extractable nickel. The result was an increase in the proportion of nickel in the exchangeable form with increasing depth in the soil profile from 5% in the 5-10cm profile to 42% in the 35-50cm profile (Figure 6.14).

At site SRG the proportion of nickel associated with the residual and iron oxide phases increased with depth, from 62% at 0-5cm to 82% in the 35-50cm profile (Figure 6.14). In contrast to the results for lead, zinc and copper, a large proportion of residual nickel was not extracted by the 2M hydrochloric acid extraction for crystalline iron (Labelled FeO). Approximately equal proportions of nickel were present in the exchangeable and carbonate fractions. Available metal decreased with depth from 30% of total nickel at the top of the soil profile to 18% of the total in the lowest profile studied. The iron and manganese oxides, organic and iron oxide fractions were all associated with small proportions of nickel decreasing with depth until in the 35-50cm profile all three fractions were below the detection limit.

The low nickel concentration in the iron oxide fraction compared to the residual phase suggests that the main source of nickel in these soils is mineral as opposed to aerial deposition. Weathering processes would then explain the high concentrations of nickel in the exchangeable phase. The low concentrations of nickel observed in the iron and manganese oxides and organic matter phases of sites RB and SRG are a result of the acidic nature of these soil profiles.

Figure 6.15 Sequential Extraction of Iron and Manganese at Ringinglow, Sites RG, RB and SRG: Each graph represents the distribution of a single metal between the geochemical fractions determined by sequential extraction. The histogram bars are plotted in groups of six depicting the concentrations (6 replicates) at increasing depth in the soil profile.

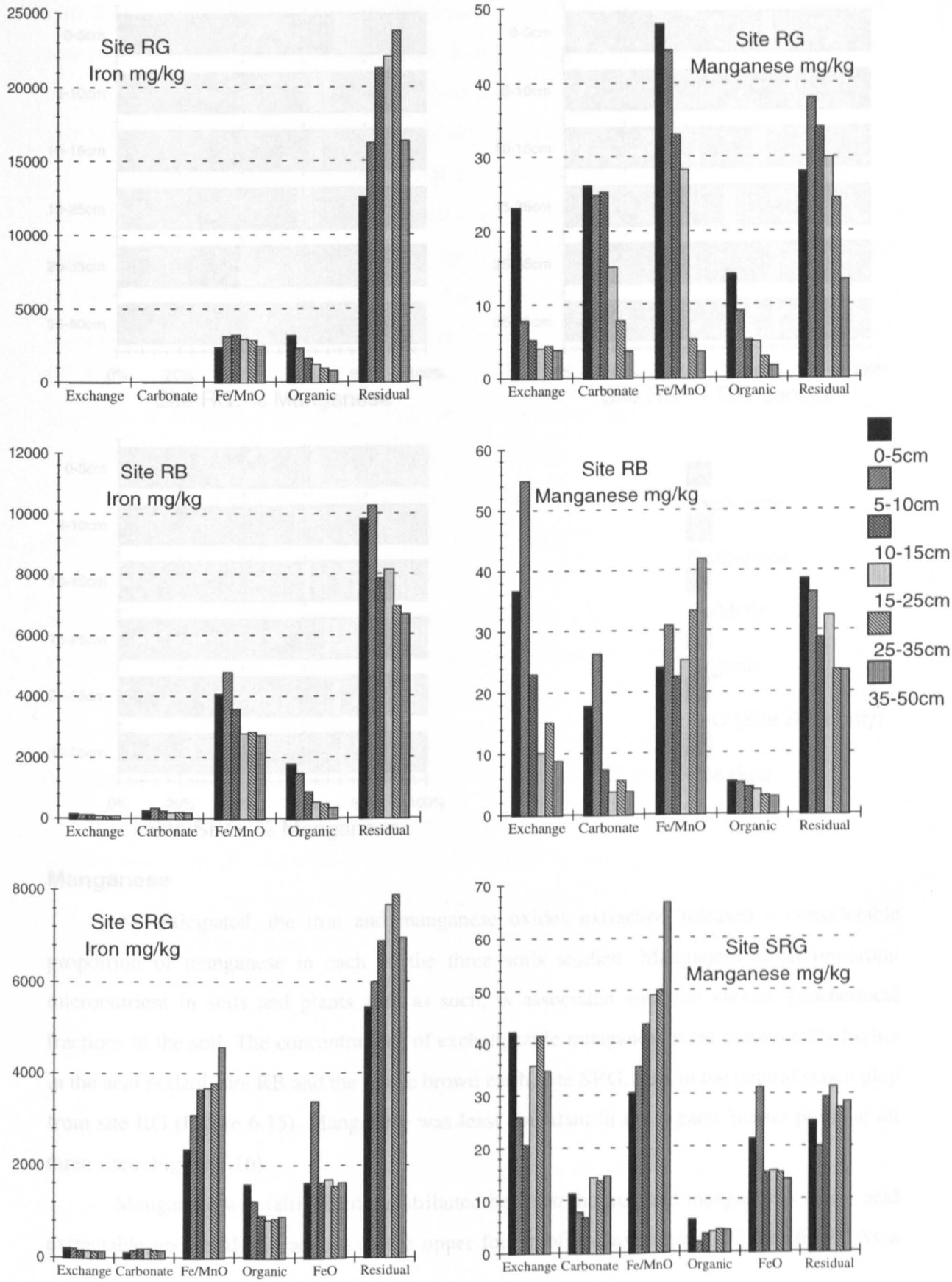
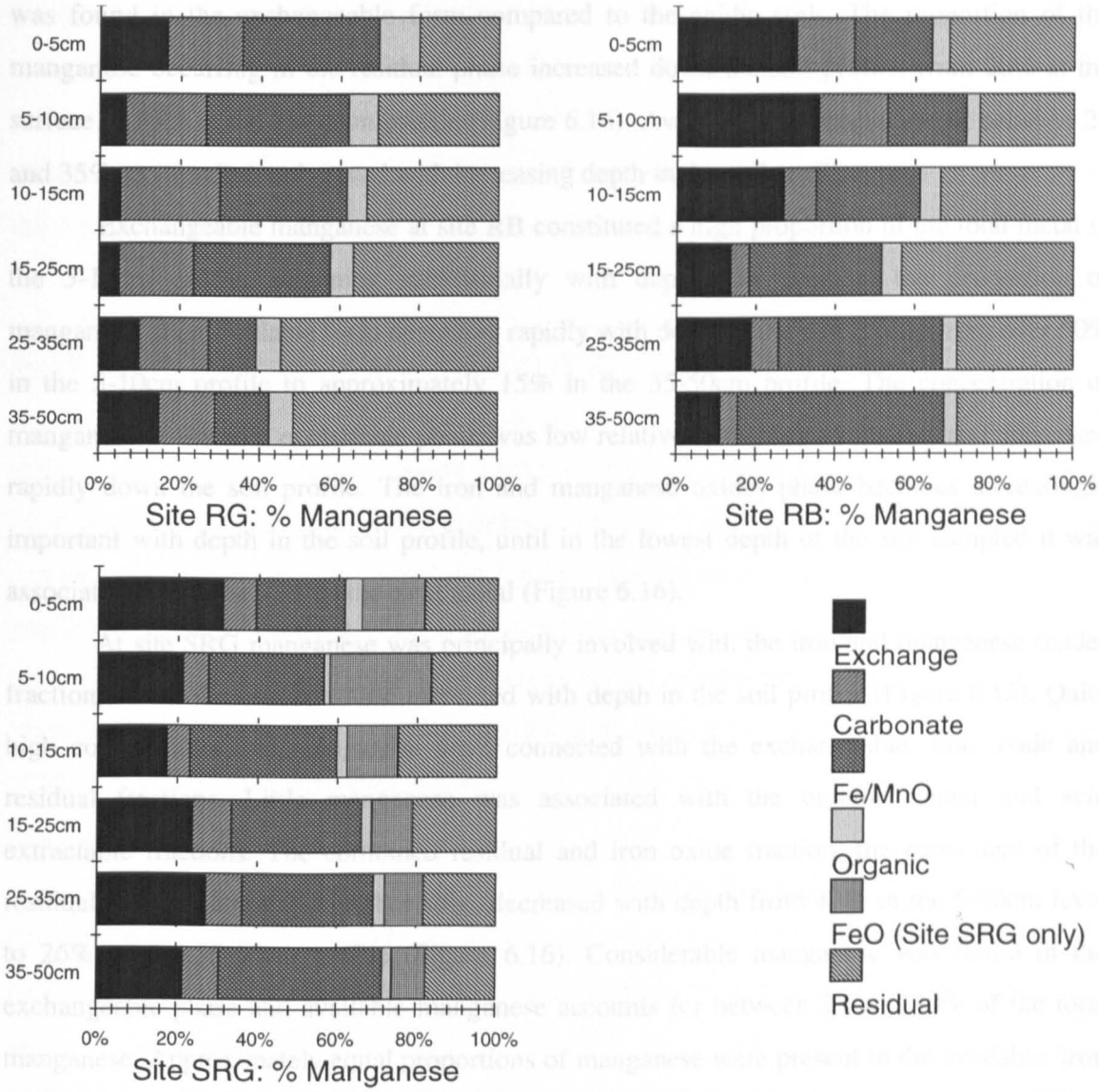


Figure 6.16 Geochemical Fractionation of Manganese at Ringinglow: Each graph illustrates the percentage of manganese in the various geochemical fractions at each depth in the soil profile, determined by sequential extraction. The y-axis is the depth in the soil profile (cm). The FeO fraction is a 2M HCl extraction for crystalline iron and was used at site SRG only.



Manganese

As anticipated, the iron and manganese oxides extraction released a considerable proportion of manganese in each of the three soils studied. Manganese is an important micronutrient in soils and plants and, as such, is associated with the various geochemical fractions in the soil. The concentrations of exchangeable manganese were considerably higher in the acid podzol, site RB and the acidic brown earth, site SRG, than in the neutral stagnogley from site RG (Figure 6.15). Manganese was least abundant in the organic matter phase at all three sites (Figure 6.16).

Manganese was fairly evenly distributed between the iron and manganese oxides, acid extractable and residual fractions in the upper four profiles investigated (Figure 6.15). As a

result of the relatively high pH of the stagnogley soil profile, around pH 6, little manganese was found in the exchangeable form compared to the acidic soils. The proportion of the manganese occurring in the residual phase increased down the soil profile, from 20% at the surface to 55% in the 25-35cm profile (Figure 6.16). Available manganese varied between 25 and 35%, no trend was observed with increasing depth in the soil profile.

Exchangeable manganese at site RB constituted a high proportion of the total metal in the 5-10cm profile, declining substantially with depth. On average, the proportion of manganese in an available form decreases rapidly with depth in the soil profile from over 50% in the 5-10cm profile to approximately 15% in the 35-50cm profile. The concentration of manganese in the acid extractable phase was low relative to the other fractions and decreased rapidly down the soil profile. The iron and manganese oxides phase becomes increasingly important with depth in the soil profile, until in the lowest depth of the soil sampled it was associated with over 50% of the total metal (Figure 6.16).

At site SRG manganese was principally involved with the iron and manganese oxides fraction, where the concentration increased with depth in the soil profile (Figure 6.15). Quite high concentrations of manganese were connected with the exchangeable, iron oxide and residual fractions. Little manganese was associated with the organic matter and acid extractable fractions. The combined residual and iron oxide fraction, the equivalent of the residual determination at the other sites, decreased with depth from 42% in the 5-10cm level to 26% in the 35-50cm profile (Figure 6.16). Considerable manganese was found in the exchangeable phase and available manganese accounts for between 23 and 40% of the total manganese. Approximately equal proportions of manganese were present in the available, iron and manganese oxides and residual fractions (including the iron oxide fraction as residual).

These results indicate that manganese was present in the soil in a number of forms including manganese oxides that were, as a proportion of the total manganese concentration, the second most important form after the residual phase.

Iron

All three soil profiles had large quantities of iron in the residual fraction, with some iron extracted in the iron and manganese oxides and organic matter fractions (Figure 6.15). In the acid podzol and acidic brown earth the iron and manganese oxides fraction contained about half the amount of iron contained in the residual phase and showed a down profile change in concentrations that is mirrored in the residual phase. Iron concentrations in the

residual phase of the neutral stagnogley were far higher than in the iron and manganese oxides phase. The exchangeable and carbonate phases contained very low concentrations of iron compared with the other fractions. The results for the 2M HCl extraction demonstrate that it is not sufficiently powerful to dissolve all of the crystalline iron oxide, leaving most of it to be dissolved in the nitric acid digest. The proportion of iron in the organic matter phase is lower than at the other sites.

6.11 Geochemical Fractionation and Soil Properties

In Chapter 5 (Table 5.5) it was shown that with the exceptions of pH and organic carbon, and pH and cation exchange capacity, the soil properties at site RG were highly intercorrelated. Similarly, the soil properties at site RB (Table 6.6), with the exception of pH and cation exchange capacity, were also highly intercorrelated, therefore, it was not normally possible to include more than one independent variable in any of the regression models for these sites. At site SRG all the soil properties tested, except organic carbon, were constant irrespective of depth in the soil profile restricting the regression analysis to models containing organic carbon as an independent variable.

Exchangeable Metal

Cation exchange capacity was constant at all three Ringinglow sites and so was not included in the regression models. Regression models of exchangeable lead, zinc, copper and nickel were tested with organic carbon content. Organic matter is an important provider of cation exchange sites. Exchangeable lead at site RB was found to be significantly associated with organic carbon (Table 6.5). The metal was either weakly complexed with organic matter, or associated with soluble organics dissolved in the aqueous extractant. The tests failed to show any significant relationships between the other exchangeable heavy metals and organic carbon content in the neutral stagnogley, site RG and the acidic brown earth, site SRG.

Table 6.5 Metals Associated with the Exchangeable Phase, Site RB

Models: Exchangeable HM = Constant + OC n=36

Exchangeable HM - heavy metals extracted in the exchangeable fraction.

Metal	Soil Property Included in the subset model	Proportion of Variance Accounted for by the Soil Properties %	Coefficient 'slope'	P (2 Tail) T-test
Lead	OC	89.5	6.4	0.000

Metal Associated with the Iron and Manganese Oxides Phase

The heavy metal concentrations in the iron and manganese oxides phase were expected to be related to the amorphous iron oxide content of the soil. In the neutral stagnogley at site RG, regression analysis showed that lead concentrations in the iron and manganese oxides phase were strongly associated with quantity of amorphous iron oxides (Table 6.6). However, organic carbon described a much larger proportion of the variation in zinc concentrations in the iron and manganese oxides phase than did amorphous iron oxides. The relationship of iron and manganese oxides occluded zinc with amorphous iron oxides was nonlinear. Amorphous iron oxides appeared to become more efficient at binding zinc when they were present at higher concentrations. The iron and manganese oxides phase was not linked with major proportions of copper or nickel and the concentrations showed little variation with increasing depth in the soil profile.

Table 6.6 Metals Associated with the Iron and Manganese Oxides Phase, Site RG

Models: FeMnO HM = Constant + PyrFe n=36

FeMnO HM = Constant + OC

FeMnO HM - heavy metals extracted in the iron and manganese oxides fraction.

PyrFe - iron extracted by a pH7 pyrophosphate extraction for amorphous iron.

Metal	Soil Properties Included in the subset model	Adjusted Squared Multiple R	Coefficient 'slope'	P (2 Tail) T-test
Lead	PyrFe	97.5	0.043	0.000
Zinc	PyrFe	63	0.009	0.000
Zinc	OC	95.6	1.58	0.000

Heavy metals present in the iron and manganese oxides fraction extracted by the sequential extraction scheme in the acid podzol at site RB were regressed with amorphous iron oxides. Lead, zinc and copper in the iron and manganese oxides phase were found to be significantly associated with amorphous iron oxides (Table 6.7). Amorphous iron oxides explained 80.5% of the variation in lead concentrations in the fraction. The low proportion of the variance in zinc and copper concentrations, in the iron and manganese oxides phase, accounted for by amorphous iron suggests that other factors are important to the speciation of those metals. The proportion of copper in the iron and manganese oxides phase was small compared to the organic and residual phases.

Table 6.7 Metals Associated with the Iron and Manganese Oxides Phase, Site RB

Models: FeMnO HM = Constant + PyrFe n=36

FeMnO HM - heavy metals extracted in the iron and manganese oxides fraction.

PyrFe - iron extracted by a pH7 pyrophosphate extraction for amorphous iron.

Metal	Soil Property Included in the subset model	Proportion of Variance Accounted for by the Soil Properties %	Coefficient 'slope'	P (2 Tail) T-test
Lead	PyrFe	80.5	0.008	0.000
Zinc	PyrFe	37.3	0.0003	0.000
Copper	PyrFe	46.8	0.00015	0.000

At site SRG, amorphous iron content did not explain a significant portion of the variance in heavy metal concentrations in the iron and manganese oxides phase. However, copper was significantly associated with organic carbon and pH (Table 6.8). These soil properties did not explain a significant proportion of the variation in the binding of the other metals to iron and manganese oxides.

Table 6.8 Metals Associated with the Iron and Manganese Oxides Phase, Site SRG

Models: FeMnO HM = Constant + pH + OC n=36

FeMnO HM - heavy metals extracted in the iron and manganese oxides fraction.

OC - Organic Carbon content.

Metal	Soil Property Included in the subset model	Proportion of Variance Accounted for by the Soil Properties %	Coefficient 'slope'	P (2 Tail) T-test
Copper	OC, pH	75.9	OC -0.327	0.000
			pH -1.148	0.017

Metals Associated with the Organic Matter Phase

Regression analysis was carried out to determine whether the variation in heavy metal concentrations in the organic matter phase of the sequential extraction scheme was explained by variation in soil organic carbon content and pH (Table 6.9). The inclusion of pH in the models was based on the pH dependence of organic matter complexation of heavy metal cations.

The pH term in the regression model did not significantly improve the regression model for any of the metals investigated at site RG. The regression models for lead, zinc and

copper with organic carbon were all significant. Organic carbon explained 96.6% of the variation in zinc and 97.7% of the variance in lead associated with the organic fraction. However, copper which was expected to be strongly associated with organic matter was only weakly related to organic carbon. A possible reason for the weak relationship between copper and carbon was that copper remains in insoluble form in the residual phase and has not become soluble, so it was not available for complexation. Nickel was not significantly related to organic carbon content.

Table 6.9 Metals Associated with the Organic Matter Phase, Site RG

Models: OM HM = Constant + OC n=35

Organic HM - heavy metals extracted in the organic fraction.

OC - Organic Carbon content.

Metal	Soil Properties Included in the subset model	Adjusted Squared Multiple R	Coefficient 'slope'	P (2 Tail) T-test
Lead	OC	97.7	5.82	0.000
Zinc	OC	96.6	1.29	0.000
Copper	OC	42.4	1.01	0.000

Over 90% of the variation of lead and copper concentrations in the organic matter phase in the acid podzol, site RB, was attributed to organic carbon (Table 6.10). These reults suggest strong complexation of these metals with organic matter. The percentages of zinc and nickel in the organic matter phase were small and no significant relationships were found between their concentrations in the organic matter phase, and organic carbon content.

Table 6.10 Metals Associated with the Organic Matter Phase, Site RB

Models: OM HM = Constant + OC n=36

Organic HM - heavy metals extracted in the organic fraction.

OC - Organic Carbon content.

Metal	Soil Property Included in the subset model	Proportion of Variance Accounted for by the Soil Properties %	Coefficient 'slope'	P (2 Tail) T-test
Lead	OC	92.9	3.07	0.000
Copper	OC	93.7	1.737	0.000

There were no significant regression relationships between the heavy metals in the organic matter phase and organic carbon content at site SRG.

6.12 Fractionation in the Ringinglow and Hallen Soil Profiles

Ringinglow Soils

Total digestion results showed clear differences in the distribution of the metals at the three sites (Figure 6.8). At sites RG, a neutral stagnogley, and RB, an acid podzol, the highest concentrations of lead were found in the surface layer. In contrast, transport of lead at site SRG had resulted in the highest concentration of lead occurring in the 15-25cm profile.

The proportion of lead in an available form was highest at the RB site, 40-50%, and lowest at the RG site, 12-35%, reflecting the acidic pH of site RB. The proportion of available lead at site SRG was between the two, at 30-45%.

The proportion of zinc in the iron and manganese oxides of the acid podzol, site RB, and the acidic brown earth, site SRG, was low compared to the neutral stagnogley soil, site RG. Similar results were obtained for the proportion of nickel associated with the iron and manganese oxides phase. The proportion of lead in this fraction was found to be approximately the same in all three soil types and the proportion of copper in the fraction was higher in the acidic soils than in the neutral stagnogley. These results are consistent with studies (described in Section 1.3) that have found zinc and lead to be retained at pH values down to pH 5.5, while lead and copper were retained to pH 3-4.

A high proportion of copper was associated with the organic matter phase in all three soil profiles, demonstrating the much higher affinity of copper for organic matter, compared to the other metals. The proportion of the heavy metals associated with the organic matter phase followed the order copper >> lead > zinc > nickel. The association of heavy metals with organic matter is discussed in more detail in Chapter 7.

The largest proportions of zinc and nickel were found in the residual phase in all three soil profiles. Lead and copper associated with the residual phase were higher in the neutral stagnogley, site RG, than in the acid podzol, site RB and the acidic brown earth, site SRG.

Hallen Wood Soil Profile

The concentrations of lead, zinc and cadmium in the Hallen wood soil profile were exceptionally high, compared to other sites. Hallen wood also differs from most other sites in the extent and nature of the acid deposition incident on the site, particularly the deposition of nitric acid from nitric acid production at the Avonmouth industrial complex. The surface layer at Hallen was discontinuous with the mineral soil, due to its very high organic matter content and concentrations of heavy metals. It was not possible to make direct comparisons between

the heavy metal geochemical fractionation at the Hallen wood and Ringinglow sites. The Ringinglow site was more typical of many other sites with moderate to high levels of heavy metal contamination. The Hallen wood site is so contaminated that it is best treated as an example of extreme heavy metal contamination.

The geochemical fractionation results for iron confirmed that the hydroxylamine reagent was selective for amorphous iron oxides and did not attack crystalline iron oxides, which were removed by the residual digestion. The determination of manganese in the iron and manganese oxides fraction allowed the proportion of manganese present in the form of manganese oxides to be estimated.

The changes in the proportions of zinc and cadmium associated with the various fractions, with depth in the soil profile, illustrates the sensitivity of these metals to pH which increased from pH 4.8, in the surface layer, to pH 7.2 in the 35-50cm profile. The proportions of lead and copper in the various fractions were relatively constant with depth in the soil profile. Similar results have been obtained in studies of heavy metal retention on amorphous iron oxides (Kinniburgh et al., 1976) and in soils (Elliott et al., 1986a) where copper and lead were retained at a lower pH than cadmium and zinc. Lead was fairly evenly distributed between the different phases, changes in the relative proportions with depth were slight.

The proportions of cadmium and zinc in the exchangeable fraction decreased with depth in the soil profile, reflecting the increasingly neutral pH with depth. The proportions of lead and copper in the exchangeable phase did not change significantly with depth. Cadmium mainly occurred in the exchangeable and acid extractable phases, demonstrating the importance of cation exchange complexation, in the speciation of cadmium. In a study of heavy metal speciation in soil solutions from Hallen and Haw woods, Bullock (1992) found a higher proportion of cadmium in soluble forms than lead, zinc or copper.

In the mineral soil, most of the copper metal was associated with the residual phase and not with the organic phase as had been expected. The behaviour of copper may be a result of competition for organic matter binding sites with the much more abundant lead. The proportion of zinc, in the residual phase of the mineral soil, increased rapidly with depth, in the 35-50cm profile the majority of zinc was in the residual phase. The adsorption of zinc, probably onto crystalline iron oxides, was favoured by the pH change with depth, from acidic to neutral. The proportion of cadmium associated with the residual phase increased with depth in the mineral soil, but was much lower than that of zinc.

7 Heavy Metals Associations with Humic Substances

7.1 Organic Matter Extractions

Three different methods were used to extract heavy metals associated with organic matter in soils: sequential extraction, an extraction method to isolate humic and fulvic acids and the parallel extraction scheme. Heavy metals associated with these fractions may be complexed with organic matter by cation exchange complexation, inner sphere or chelation complexation, outer sphere complexation, or they may originate from other geochemical phases. The complexation of heavy metals with organic matter is discussed in Section 3.3. The details of the likely types of heavy metal complexation in the organic fractions extracted by the three extraction schemes, based on the review in Section 3.3, are summarised in Table 7.1.

Table 7.1 Complexation Mechanisms Associated with Chemical Extraction Schemes

The types of heavy metal complexes extracted in the various organic fractions of the sequential, organic matter and parallel extraction schemes.

Extraction Scheme	*Organic Fraction*	*Extractant*	*Complexation Mechanism*
Sequential	Exchangeable	$MgCl_2$ pH 7.0	Exchangeable
	Organic	H_2O_2 / 0.02M HNO_3	Inner / Outer Sphere Complexed
Organic Matter	Humic Acid (HA)	0.1M $Na_4P_2O_7$	Inner Sphere Complexed
	Fulvic Acid (FA)	0.1M $Na_4P_2O_7$	Inner Sphere Complexed
Parallel	Humics (HU)	0.1M NaOH	Inner / Outer Sphere Complexed

The exchangeable fraction of the sequential extraction scheme contains heavy metals associated with the exchange sites of various substrates including organic matter. The exchangeable extraction may also solubilise some fulvic acids, since they are soluble in both acid and alkaline aqueous solutions. In the organic fraction of the sequential extraction scheme, metals complexed as inner sphere complexes are released during hydrogen peroxide digestion of organic matter. The oxidising sequential extraction of organic matter is unlikely to extract other phases significantly, particularly given that the exchangeable, acid extractable and iron and manganese oxides fractions are extracted before the organic matter phase.

In the organic matter extraction, humic substances were isolated using 0.1M potassium pyrophosphate (Chapter 3), these were then digested to determine their heavy metal content.

The long multi-step extraction scheme and in particular the acid precipitation of humic acid, are almost certain to result in the removal of exchangeable and outer sphere complexed heavy metals from the humic substances. Heavy metal concentrations in the humic extracts may, therefore, be considered to be inner sphere complexed by chelation complexation. The complexity of the extraction scheme leads to the accumulation of inaccuracies. To check the accuracy of the results obtained by the isolation of humic substances a different scheme was devised.

The parallel extractions were carried out using a range of extractants that are commonly used in soil chemical analysis. Each extraction was carried out on a fresh soil sample, hence the term parallel extraction, removing the possibility of cumulative errors present in the other schemes. In the parallel extraction scheme a 0.1M sodium hydroxide extraction was used to extract organic matter, whilst leaving the other geochemical fractions relatively undisturbed. The high pH of the dilute sodium hydroxide solution reduces the extraction of metals from cation exchange sites to a minimum. Heavy metals extracted by the parallel extraction of humic substances were most likely to be from outer sphere complexes and inner sphere complexes. The extraction of organic matter in the sequential extraction scheme was carried out in nitric acid at 85°C and as a consequence should be a stronger extractant than 0.1M sodium hydroxide.

The results of these extractions, for lead, zinc, cadmium and copper at Hallen, site HA were compared to determine the association of these metals with the different components of organic matter. At Ringinglow the distribution of the metals lead, zinc, copper and nickel were compared to investigate:

(i) associations of different metals with organic matter in each single soil profile,

(ii) differences between soil profiles in the binding of a single metal to organic matter.

In a single soil profile differences of the distribution of the metals will be a function of their chemistry. Differences in the distribution of a metal in the three different soil profiles, RG, RB, and SRG will be due to the effects of soil properties on the associations of the metal with the various components of organic matter.

7.2 Heavy Metal Concentrations in Organic Matter at Hallen

The soil profile at Hallen has a 0-5cm litter layer with an organic matter content that was far in excess of the other profile depths (loss on ignition determination 68%). The concentrations of lead, zinc and copper at the top of the soil profile were likewise far higher

than those in the lower profile depths. There was clearly a discontinuity between the litter layer and the mineral soil below it. The aim of the present study was to investigate heavy metal speciation in mineral soil profiles, so to make the changes in metal distributions with depth in the soil profile easier to interpret, this litter layer profile has been omitted from the analysis.

Lead

The concentration of lead was much higher in the sequential extraction organic matter phase than in the other fractions (Figure 7.1). Given that exchangeable lead had already been removed in the exchangeable fraction, lead in the organic fraction was either inner or outer sphere complexed to organic matter. The distribution of the metal down the profile in the sequential extraction organic matter phase was similar to that in the humics extracted by the parallel extraction. Lead concentrations in the humic acid isolated from the organic matter extraction were very low, except in the 5-10cm profile. Metal concentrations in fulvic acid were very low, ranging from 0.7-1.0 mg/kg. The concentrations of lead associated with humic substances were small in comparison to the levels found in the sequential extraction organic matter phase. As a result, it seems likely that lead was complexed by outer sphere complexation. However, the levels of lead present in the sequential organic fraction were surprisingly high relative to the other fractions.

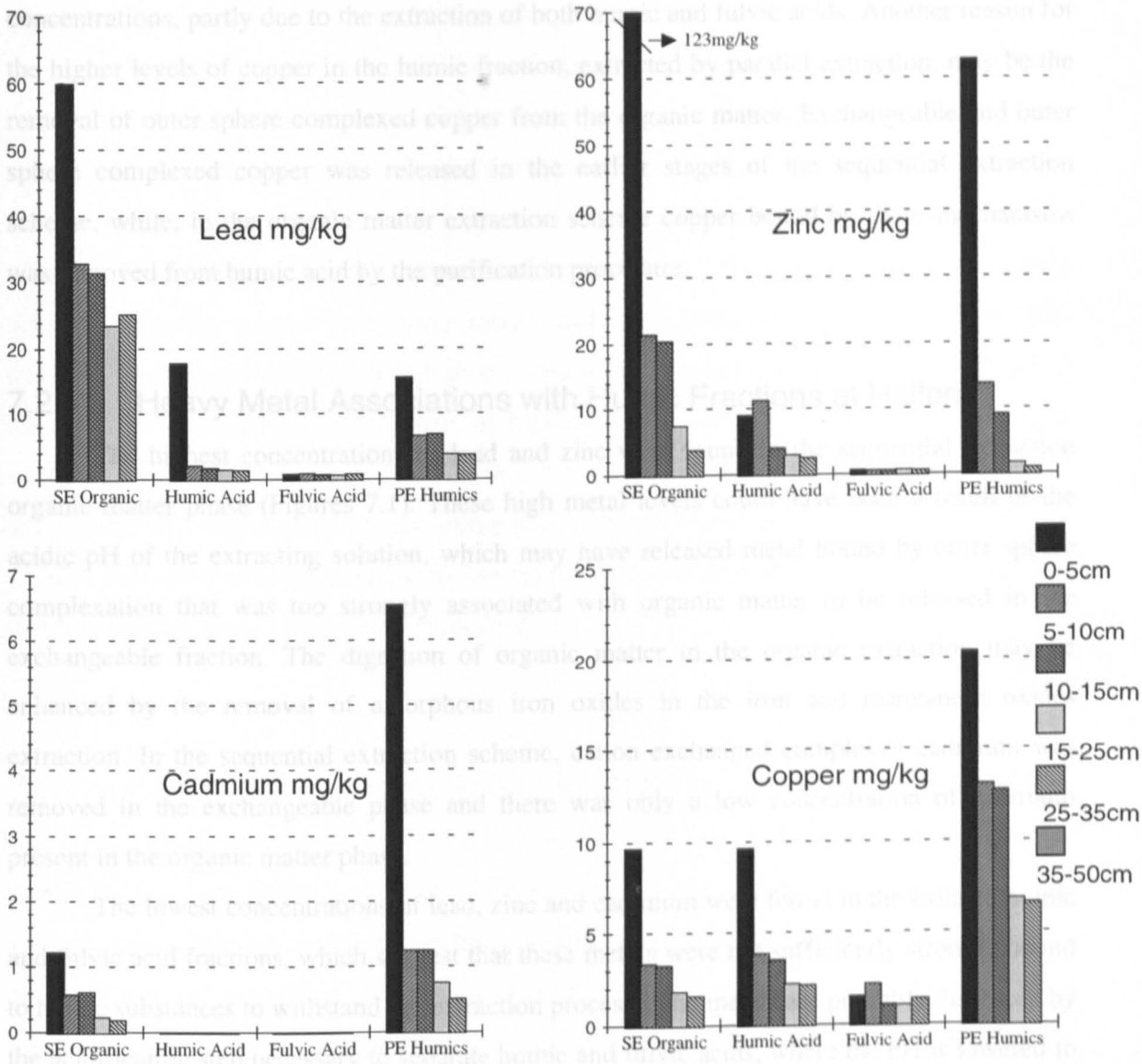
Zinc

Like lead, zinc concentrations were highest in the organic matter phase of the sequential extraction scheme. Zinc concentrations in the parallel extraction humics fraction were about half those of the sequential extraction phase. Both schemes show a similar decrease in metal concentration with depth in the soil profile (Figure 7.1). Fulvic acid zinc concentrations were around 0.5mg/kg at all depths in the soil profile. At lower depths in the soil profile, in particular the 25-35cm and 35-50cm layers, there was some evidence that inner sphere complexation was the main mechanism of metal complexation with organic substances, with similar concentrations of zinc in all three extractions.

Cadmium

In contrast to the results for lead and zinc, the concentration of cadmium in the parallel extraction humic fractions was higher than in the sequential extraction organic matter fraction (Figure 7.1). Cadmium occurring in exchange sites on organic matter will be released in the exchangeable fraction of the sequential extraction scheme, rather than in the organic matter phase, and a high proportion of cadmium was found to be in exchangeable form. In the parallel

Figure 7.1 Heavy Metals in the Organic Matter Fractions at Hallen, site HA: in the sequential extraction (SE) organic fraction, isolated humic acid, isolated fulvic acid and the parallel extraction (PE) humic fraction. The histogram bars are plotted in groups of six depicting the heavy metal concentrations (mean 6 replicates) at increasing depth in the soil profile.



extraction of humic substances, some of the exchangeable cadmium may be released together with outer and inner sphere complexed cadmium giving the high values observed. No cadmium was detected in the humic and fulvic acid extracts isolated from the organic matter extraction.

Copper

The concentrations of copper in the organic phase of the sequential extraction and in humic acid extracted by the organic matter extraction were almost identical at all depths in the soil profile (Figure 7.1). Copper in both these extractions was almost certainly inner sphere complexed to humic acids. The copper concentrations in the parallel extraction humic fraction

shows the same trend down profile as the other extractions, but with higher metal concentrations, partly due to the extraction of both humic and fulvic acids. Another reason for the higher levels of copper in the humic fraction, extracted by parallel extraction, may be the removal of outer sphere complexed copper from the organic matter. Exchangeable and outer sphere complexed copper was released in the earlier stages of the sequential extraction scheme, while, in the organic matter extraction scheme copper bound by these mechanisms was removed from humic acid by the purification procedure.

7.2.1 Heavy Metal Associations with Humic Fractions at Hallen

The highest concentrations of lead and zinc were found in the sequential extraction organic matter phase (Figures 7.1). These high metal levels could have been a result of the acidic pH of the extracting solution, which may have released metal bound by outer sphere complexation that was too strongly associated with organic matter to be released in the exchangeable fraction. The digestion of organic matter in the organic extraction may be enhanced by the removal of amorphous iron oxides in the iron and manganese oxides extraction. In the sequential extraction scheme, cation exchanged complexed cadmium was removed in the exchangeable phase and there was only a low concentration of cadmium present in the organic matter phase.

The lowest concentrations of lead, zinc and cadmium were found in the isolated humic and fulvic acid fractions, which suggest that these metals were not sufficiently strongly bound to humic substances to withstand the extraction process. The metals are probably displaced by the acidification step necessary to separate humic and fulvic acids, where the pH is lowered to pH 2. Other studies have shown that zinc and cadmium have relatively low affinities for humic substances compared to lead and copper (Stevenson, 1976; and Stevenson, 1977). The low concentration of lead associated with humic acid is surprising given the high affinity of the metal for humic substances reported by most studies, e.g. Schnitzer (1969), Stevenson, (1976), and Stevenson, (1977). It is also possible that there was simply no significant inner sphere complexation of these metals.

Copper has a very high affinity for humic and fulvic acids (Schnitzer, 1969). The virtually identical concentrations of copper in the organic phase of the sequential extraction scheme and the humic acid fraction of the organic matter extraction suggest that both extractions have removed inner sphere complexed copper from humic acids. Copper

associated with fulvic acids may have been solubilised in the early stages of the sequential extraction scheme, before the organic extraction.

Concentrations of lead and zinc in the humic substances extracted by parallel extraction were intermediate between those in the humic acid and organic matter fractions. In contrast to lead and zinc, both cadmium and copper were found at highest concentrations in the humic fraction of the parallel extraction. The alkaline parallel extraction may be less efficient at extracting outer sphere complexed lead and zinc. The parallel extraction of humic substances should remove both outer sphere and inner sphere complexed cadmium. The amphoteric chemical nature of cadmium may result in its partial dissolution at the high pH of the 0.1M sodium hydroxide extraction of humics. The result would then be low levels of cadmium in the sequential extraction organic matter phase relative to the parallel extraction humic fraction. The higher copper concentration in the humic substances extracted by the parallel extraction scheme, relative to the copper concentration in humic acids, is partly a result of the less specific extraction procedure.

7.3 Heavy Metal Concentrations in Organic Matter at Ringinglow

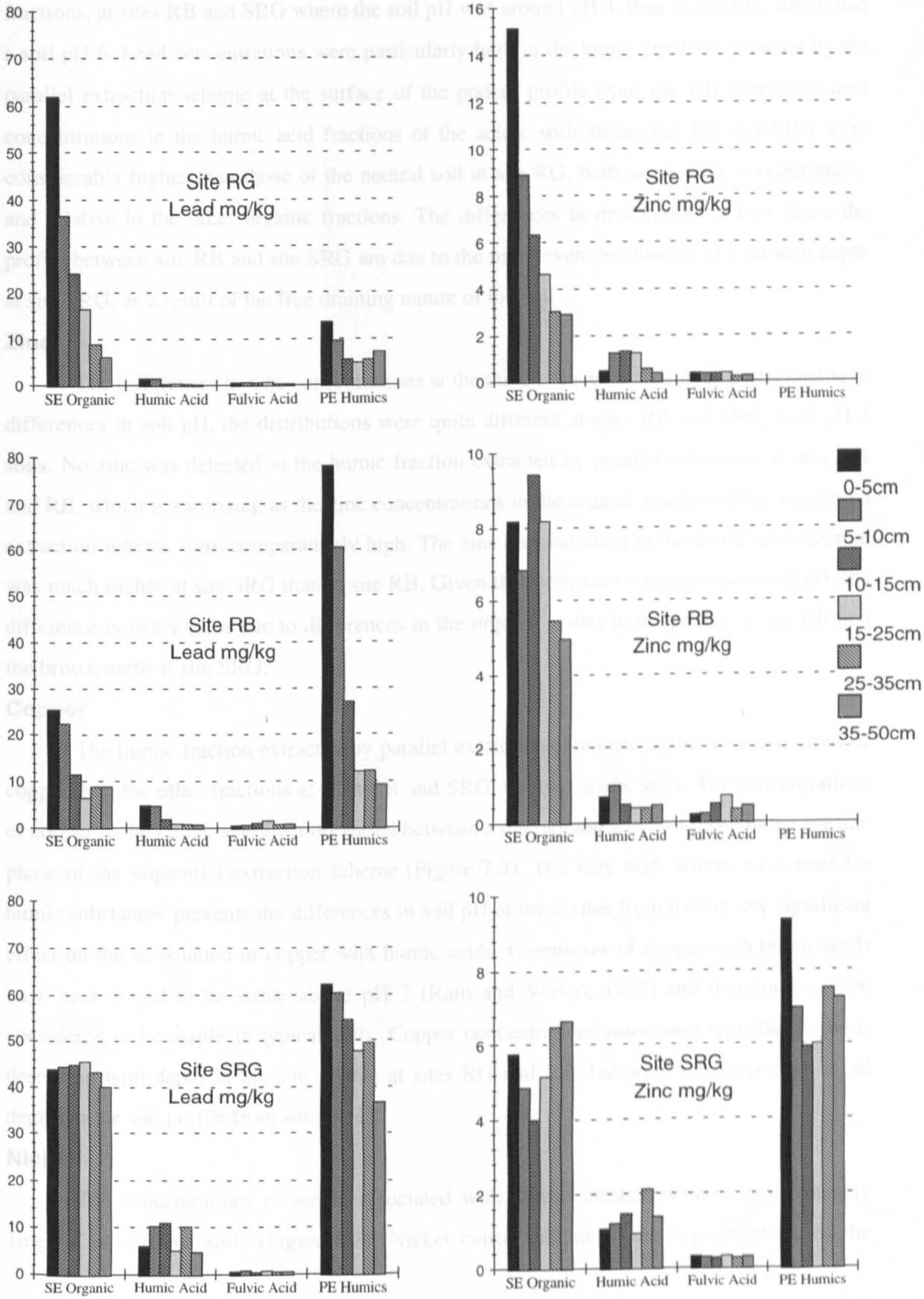
The graphs plotted in Figure 7.2 and Figure 7.3 illustrate differences in the absolute concentrations and relative proportions of lead, zinc, copper and nickel associated with the various organic fractions isolated from the soil samples. With the exception of zinc, the graphs of a single metal at each of the three sites are plotted with the same y-axis scale to allow comparison of the metal distributions at the different sites. Where there are no bars plotted, the metal concentrations were below the detection limit.

The most important difference between the three sites was the soil pH, which is illustrated in Figure 6.1. The pH at site RG, a neutral stagnogley was around pH 6, the pH at both sites RB, an acid podzol, and SRG, an acidic brown earth, was pH 4 with very little change in pH with increasing depth. A difference of pH 2 is equivalent to a difference in the hydrogen ion concentration of 100 fold.

Lead

There are clear differences in the association of lead with the organic fractions at the different sites (Figure 7.2). The main differences in the lead distributions in the organic fractions are between site RG and sites RB and SRG. The lead concentrations in the humic

Figure 7.2 Lead and Zinc in the Organic Matter Fractions at Ringinglow: in the sequential extraction (SE) organic fraction, isolated humic acid, isolated fulvic acid and the parallel extraction (PE) humic fraction. The histogram bars are plotted in groups of six depicting the heavy metal concentrations (mean 6 replicates) at increasing depth in the soil profile.



fractions extracted by the parallel extraction scheme were much higher, relative to the other fractions, at sites RB and SRG where the soil pH was around pH 4, than at site RG, which had a soil pH 6. Lead concentrations were particularly high in the humic fraction extracted by the parallel extraction scheme at the surface of the podzol profile from site RB. Similarly, lead concentrations in the humic acid fractions of the acidic soils from sites RB and SRG were considerably higher than those of the neutral soil at site RG, both as absolute concentrations and relative to the other organic fractions. The differences in distribution of lead down the profile between site RB and site SRG are due to the more even distribution of lead with depth at site SRG, as a result of the free draining nature of the soil.

Zinc

The differences in zinc concentrations at the three sites were not directly attributable to differences in soil pH, the distributions were quite different at sites RB and SRG, both pH 4 soils. No zinc was detected in the humic fraction extracted by parallel extraction at sites RG and RB, which is surprising as the zinc concentrations in the organic fraction of the sequential extraction scheme were comparatively high. The zinc concentration in the humic acid fraction was much higher at site SRG than at site RB. Given that both sites have the same soil pH, the difference is likely to be due to differences in the organic matter in the podzol at site RB and the brown earth at site SRG.

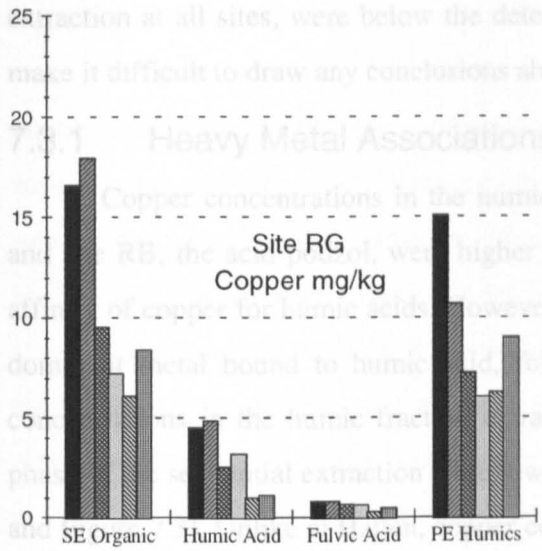
Copper

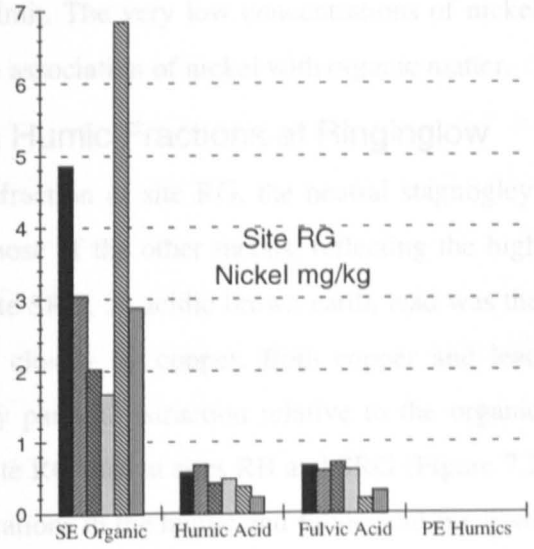
The humic fraction extracted by parallel extraction contained higher concentrations of copper than the other fractions at sites RB and SRG, the two acidic soils. The concentrations of copper in the humic acid fraction varied between a quarter and a half of those in the organic phase of the sequential extraction scheme (Figure 7.3). The very high affinity of copper for humic substances prevents the differences in soil pH at these sites from having any significant effect on the association of copper with humic acids. Complexes of copper with humic acids have been found to be stable above pH 2 (Ram and Verloo, 1985) and therefore may be considered to be stable in typical soils. Copper concentrations associated with humic acids decreased with depth in the soil profile at sites RG and RB, but were relatively high at all depths in the soil profile from site SRG.

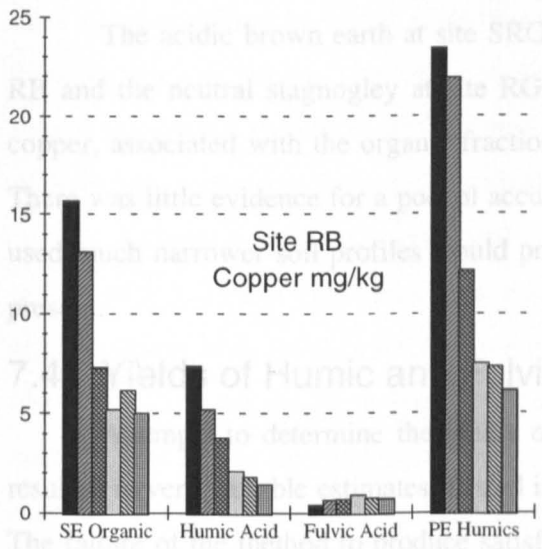
Nickel

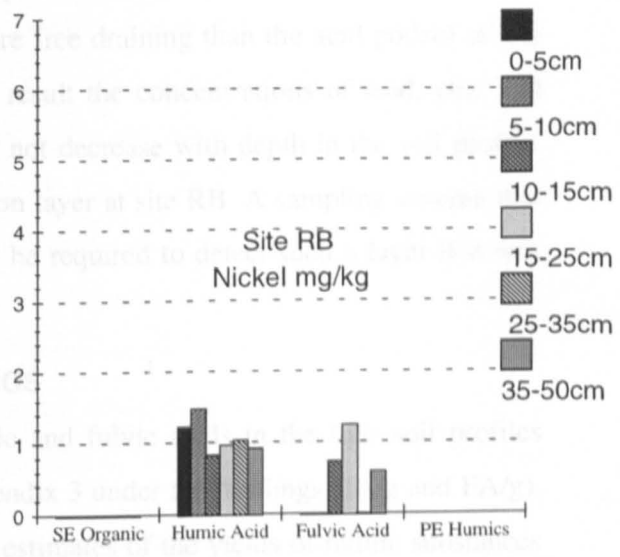
The concentrations of nickel associated with humic substances were approximately 1mg/kg in all three soils (Figure 7.3). Nickel concentrations in the organic phase of the

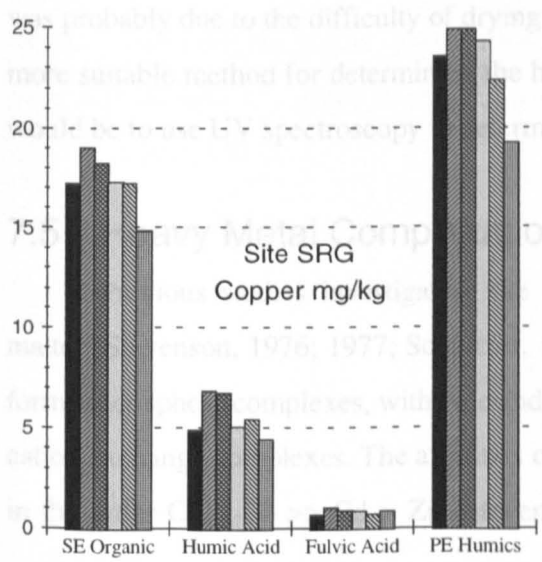
Figure 7.3 Copper and Nickel in the Organic Matter Fractions at Ringinglow: in the sequential extraction (SE) organic fraction, isolated humic acid, isolated fulvic acid and the parallel extraction (PE) humic fraction. The histogram bars are plotted in groups of six depicting the metal concentrations (mean 6 replicates) at increasing depth in the soil profile.

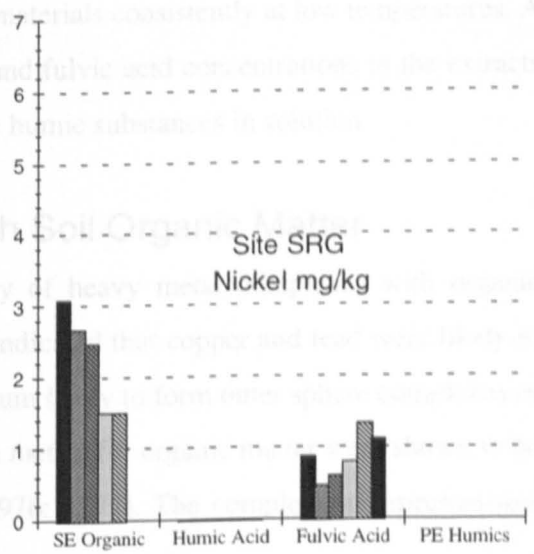












sequential extraction scheme at site RB and in the humic fraction extracted by parallel extraction at all sites, were below the detection limit. The very low concentrations of nickel make it difficult to draw any conclusions about the association of nickel with organic matter.

7.3.1 Heavy Metal Associations with Humic Fractions at Ringinglow

Copper concentrations in the humic acid fraction of site RG, the neutral stagnogley, and site RB, the acid podzol, were higher than those of the other metals, reflecting the high affinity of copper for humic acids. However, at site SRG, an acidic brown earth, lead was the dominant metal bound to humic acid, followed closely by copper. Both copper and lead concentrations in the humic fraction extracted by parallel extraction relative to the organic phase of the sequential extraction were lower at site RG than at sites RB and SRG (Figure 7.2 and Figure 7.3). Unlike at Hallen, copper concentrations in the humic and fulvic acid fractions are lower than those in the organic phase of the sequential extraction scheme.

The acidic brown earth at site SRG is more free draining than the acid podzol at site RB and the neutral stagnogley at site RG. As a result the concentrations of lead, zinc and copper, associated with the organic fractions, did not decrease with depth in the soil profile. There was little evidence for a podzol accumulation layer at site RB. A sampling scheme that used much narrower soil profiles would probably be required to detect such a layer if it was present.

7.4 Yields of Humic and Fulvic Acids

Attempts to determine the yields of humic and fulvic acids in the four soil profiles resulted in very variable estimates (Listed in Appendix 3 under the headings HA/g and FA/g). The failure of the method to produce satisfactory estimates of the yields of humic substances was probably due to the difficulty of drying these materials consistently at low temperatures. A more suitable method for determining the humic and fulvic acid concentrations in the extracts would be to use UV spectroscopy to determine the humic substances in solution.

7.5 Heavy Metal Complexation with Soil Organic Matter

Previous studies investigating the stability of heavy metal complexes with organic matter (Stevenson, 1976; 1977; Schnitzer, 1969) indicated that copper and lead were likely to form inner sphere complexes, with zinc and cadmium likely to form outer sphere complexes or cation exchange complexes. The affinities of these metals for organic matter were shown to be in the order Cu > Pb >> Cd > Zn (Stevenson, 1976: 1977). The complexation mechanisms

responsible for complexing heavy metals in the various fractions of the sequential, parallel and organic matter extraction schemes are outlined in Table 7.1.

In the brown earth from Hallen, copper was found to be strongly associated with humic acid by inner sphere complexation. However, contrary to expectations, lead did not appear to be associated with organic matter by inner sphere complexation. The acidification step in the organic matter extraction scheme is probably sufficiently powerful to remove the lead, which has a lower affinity for humic substances than copper, from humic acids. The results suggested that the high levels of lead and zinc in the organic phase of the sequential extraction scheme were bound by outer sphere complexation, as anticipated in the case of zinc. Cadmium was probably bound to exchange sites on the organic matter and was released in the exchangeable phase of the sequential extraction scheme.

At Ringinglow, copper was complexed by inner sphere complexation and was found to have a higher affinity for humic acids than the other metals. The results for lead were similar to those obtained at Hallen. Lead did not appear to be associated with organic matter by inner sphere complexation. The results for lead and zinc indicated that outer sphere complexation with organic matter was the most important binding mechanism for these metals.

Comparison of the heavy metal concentrations in the different organic fractions does not produce any clear cut results. There is still no satisfactory way of extracting unmodified organic matter from soils, or determining the heavy metal content of specific organic fractions. However, these results do at least show that there are clear differences between the heavy metals that relate to their chemical properties. In particular, the humic fraction of the organic matter extraction contains very low concentrations of heavy metals with the exception of copper. The extraction and purification procedure is sufficiently powerful to remove all the heavy metals from the humic substances with the exception of copper. The results confirm the very high affinity of copper to humic substances reported in the literature (Stevenson, 1976; and Stevenson, 1977).

8 Conclusion

8.1 Heavy Metal Speciation in a Soil Profile from Hallen Wood

The Hallen wood site is unique in the UK, in the levels of metal contamination found in the surface layers of the soil and because it receives both nitric and sulphuric acid deposition from the industrial complex at Avonmouth. The very high concentrations of all four heavy metals in the organic surface layer, compared to the mineral soil, demonstrated the capacity of organic matter to immobilise these metals. The most important soil property in the brown earth profile from Hallen, site HA, was pH which changed from an acidic surface profile, pH 4.8, to a neutral/alkaline soil at 35-50cm depth, pH 7.2.

There was a noticeable change in the geochemical fractionation of zinc with depth in the soil profile, with a shift from available to residual forms corresponding to the change in pH. The high proportion of cadmium in the exchangeable phase suggested that it was more mobile than zinc, in contrast to most other studies that have shown zinc to be more mobile than cadmium (Campbell et al., 1983; Scokart et al., 1983). These results may be a consequence of the much greater concentrations of lead and zinc present at the site which have a higher affinity for geochemical phases that would otherwise be associated with cadmium. The saturation of the less available phases with lead and zinc leads to a higher proportion of cadmium being in easily available forms than would otherwise be the case.

Lead and copper were much more effectively immobilised in the Hallen wood soil profile than cadmium and zinc. Studies of the retention of lead and copper on amorphous iron oxides in laboratory studies (Kinniburgh et al., 1976) and in studies of whole soils (Elliott et al., 1986a) have shown that lead and copper are retained at lower pH values than zinc and cadmium. In the mineral soil, lead was more evenly distributed between the geochemical phases than the other heavy metals, with only minor changes in the proportions of the metal found in the different phases with depth.

Aerial deposition of copper was very effectively immobilised by the surface organic layer, through complexation with organic matter. The behaviour of copper in the mineral soil below the 0-5cm organic surface layer was different to that observed by other studies, where copper has been found to be strongly associated with the organic matter phase (Griffin et al., 1989). The strong association of copper with the residual phase may be a result of competition with the high concentration of lead in the soil. It may also reflect that copper in the mineral

soil was probably derived from mineral weathering, rather than aerial deposition and was not mobilised in the soil to react with organic matter.

The mobilisation of cadmium and zinc at Hallen wood has been demonstrated in a long term study by Martin and co-workers and was reviewed in Martin and Bullock (1994). Total digestions of soil samples from different depths in the soil profile at Hallen and Haw woods showed mobilisation of cadmium and zinc has been taking place over the last two decades at the site. The geochemical fractionation results obtained in the present study are similar to those obtained by Bullock (1992), using completely different extraction methods. The results demonstrate the reliability of the sequential extraction schemes which were then applied to the three soil types from the Ringinglow site.

8.2 Heavy Metal Speciation in Soil Profiles from Ringinglow

The determination of the geochemical fractionation of heavy metals, in three soil profiles from the same area, receiving the same metal input, allowed differences in their speciation to be attributed to differences between the three different soil types, rather than variation in other environmental conditions. The most important differences between these soil profiles were in their pH profiles, which had a very significant effect on the geochemical fractionation of heavy metals.

Total metal concentrations in the three soils were very different. In the acid podzol, site RB and neutral stagnogley, site RG, lead and zinc concentrations decreased with depth in the soil profile. However, in the acidic brown earth, site SRG, the total lead concentration was highest in the 10-15cm profile, suggesting that lead had been transported down the soil profile, possibly as a result of the acid pH and free draining nature of the soil.

There were clear differences in the speciation of lead, in the three soil types, relating to soil pH. The proportion of available lead was 12-35% in the neutral stagnogley, site RB, 40-50% in the acid podzol, site RB and 30-45% in the acidic brown earth profile, site SRG. These results confirm that the proportion of lead in an available form was higher in acidic soils than neutral soil. Similar trends were obtained for zinc and copper.

The proportions of the heavy metals associated with the iron and manganese oxides phase were examined in relation to the soil type. In the acid podzol and acidic brown earth the proportions of zinc and nickel were much lower than those found in the neutral stagnogley soil profile. However, the proportions of lead and copper in the phase did not vary appreciably with soil type. These results were consistent with the affinities of heavy metals for the iron

and manganese oxides fraction determined by Kinniburgh et al. (1976), as was the case in the brown earth profile from Hallen wood.

Unlike copper in the soil profile from Hallen wood, copper in all three soil profiles from Ringinglow was strongly associated with the organic matter phase to a much greater extent than lead, zinc and nickel. The proportion of the heavy metals associated with organic matter followed the order copper > lead > zinc > nickel.

The residual phase was associated with the highest proportions of zinc and nickel in all three soil types. Higher concentrations of lead and copper were associated with the residual phase in the neutral stagnogley, site RG than in the acid podzol, site RB and the acidic brown earth, site SRG.

8.3 Organic Matter Complexation of Heavy Metals

The results indicated that consideration of the types of humic substances: humic acids and fulvic acids, did not help to explain the observed patterns in the heavy metal concentrations associated with these substances in the different extractions as much as the type of complexation. The complexation mechanisms responsible for complexing heavy metals in the various fractions of the sequential, parallel and organic matter extraction schemes were based on a review of the literature in Section 3.3. Heavy metal affinities for organic matter have been shown to be in the order Cu > Pb >> Cd > Zn (Stevenson, 1976: 1977). Previous studies (Schnitzer, 1969; Stevenson, 1976; 1977) indicated that copper and lead were likely to form inner sphere complexes and zinc and cadmium were likely to form outer sphere complexes or cation exchange complexes.

At Hallen, the results of the three extractions indicated that copper was complexed to humic acids by inner sphere complexation. Similar results were anticipated for lead, but the acidification step of the organic matter extraction almost certainly released lead, which has a lower affinity for humic substances than copper, from complexes with humic acids. The results for zinc were consistent with the prediction of outer sphere complexation as the main mechanism of complexation to organic matter. The results indicated that the main mechanism by which cadmium was associated with organic matter was cation exchange complexation.

The results for the three soil profiles at Ringinglow demonstrate the high affinity of copper for humic acids. The relative concentrations of copper in the humic acid extract and the organic matter phase of the sequential extraction scheme suggest that inner sphere complexation was an important process in the association of copper with organic matter. In

the neutral stagnogley, site RG, and the acid podzol, site RB, soils from Ringinglow, copper concentrations in the humic acid fraction were higher than those of other metals, a result of the high affinity of copper for humic substances. Outer sphere complexation with organic matter was the most important binding mechanism for lead and zinc. Nickel concentrations in the organic fractions were too low for any conclusions to be drawn regarding the interaction of nickel and organic matter.

The results demonstrate the difficulty of determining heavy metal associations with organic matter in soils. The extraction techniques, used to isolate humic substances, tend to release heavy metals during the acidification step needed to separate humic and fulvic acids. Copper, which has the highest affinity for humic substances, appeared to be the only metal retained through the organic matter fractionation scheme. To improve the understanding of heavy metal associations with organic matter much further work will be required investigating the complexation of heavy metals with specific functional groups on soil derived humic substances. Although it presents considerable experimental difficulties, the extraction of humic substances from soils, for detailed determination of their complexation with heavy metals, provides a more representative picture of their behaviour in the soil environment than the study of synthetic humic material. Rather than trying to examine the behaviour of heavy metals complexed to humic substances in the soil, where the extraction technique may remove the less strongly bound metals, it may be more effective to remove these metals and then experiment with the complexation of heavy metals with these purified metal free humic substances.

8.4 Relating the Geochemical Fractionation of Heavy Metals to the Soil Properties of the Soil Profile

The speciation of heavy metals in soils was strongly influenced by soil pH, both in the soil profile from Hallen wood and in the three soil profiles from Ringinglow. However, although some significant relationships between the other soil properties of the soil profiles and the geochemical fractionation of heavy metals were determined, no clear general patterns emerged from the multiple regression analysis. The multi-component nature of the soil and competition between the heavy metals for soil components make simple relationships between soil properties and heavy metal concentrations in particular phases unlikely.

One possibility to attempt to improve the understanding of the system would be to construct a geochemical model of heavy metal interactions with the soil components.

However, to do this successfully a much larger data set would be needed, together with a more detailed description of the soil profile and further studies of the interactions of heavy metals with amorphous iron and manganese oxides and organic matter. In particular geochemical modelling would require the detailed determination of anion and cation concentrations in the soil.

A recent study by Wang et al. (1995) examined evidence of complete retention of lead from atmospheric deposition in the Hubbard Brook Experimental Forest, USA. The study used lysimeters and measured lead concentrations in the streamwater and groundwater, demonstrating that lead was completely retained in the mineral layers of the soil profile. The concentrations of lead in the soil solution below the surface O horizon were 5 parts per billion compared to less than 10 parts per trillion in the streams. The analysis of lead speciation in the soil solutions showed that lead was mobilised from the surface horizons by association with mobilising colloids and partitioning of lead ions between aqueous and solid phases. The combination of this type of study with a geochemical fractionation scheme to determine which soil components immobilised the lead and a knowledge of the nature of the soil profile would be a significant improvement on the current state of knowledge.

The long term fate of the heavy metals in environment clearly depends on their fluxes. Although the heavy metal concentrations in soils are frequently quite high enough to be determined by flame atomic absorption spectrophotometry, the determination of heavy metal fluxes presents major difficulties due to the very low concentrations of metals that need to be determined, requiring the use of techniques such as ICPMS and clean laboratory facilities.

Competition between heavy metals for the sometimes limited number of specific binding sites on organic matter, iron and manganese oxides and other geochemical phases is clearly of consequence. Although studies of heavy metal associations with specific geochemical phases are important, to improve our understanding of metal speciation in soils it will be necessary to investigate the interactions of the metals with all the geochemical phases in the soil. Studies of specific soil components are most useful where they are carried out on field collected material and when the results can be directly related to the overall speciation of heavy metals in the soil. The combination of these approaches is needed to enhance our understanding of the processes and mechanisms that control the speciation of heavy metals in soils.

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Appendix 1

Soil Profile Descriptions

Hallen Wood, Berwick Ridge, Avonmouth

Description of Berwick Ridge site (OS:553 801)

Elevation: 60m

Slope: 16%, facing south-west

Vegetation: Deciduous woodland

Soil Type: Brown Earth, Worster series

Soil Survey of England and Wales description: Non calcareous reddish clay soils. Argillic pelosol

Parent material: Triassic Rhaetic clay

Depth	Characteristics
	Litter Layer: The litter layer of deciduous leaves was upto 5cm deep.
0-5cm	Very dark brown (10YR 3/2)stoneless layer of organic matter, acidic pH 4 to pH 5, many fine roots.
5-50cm	Boundary smooth and clearly defined Stoneless clay of colour 5YR 3/4 dark reddish brown, few fine roots.

The litter and fermentation layers were very thick. The high levels of metal present in these layers almost certainly reduce the rate of decomposition. The litter (L), fermentation (F), humus (H) and mineral (M) layers were well defined at this site.

Ringinglow, SW Sheffield

Site RG

Elevation: 350m

Vegetation: Heather, grass

Soil Type: Cambic Stagnohumic Gley soil

Soil Survey of England and Wales description: Wilcocks 1 association

Parent Material: Paleozoic and Pre-Cambic mudstones, slates and sandstones

Notes: Drainage at this site was comparatively poor. The site is adjacent to the Ringinglow bog site studied by Markert and Thornton (1983).

Depth	Characteristics
	Litter layer composed of decomposing heather and grass, 2cm thick.
0-15cm	Colour brown to dark brown, (10YR 4/2), stoneless humified peat, many fine roots throughout depth.
15-50cm	Slightly stoney clay, somewhat plastic consistence, weathered sandstone fragments, colour greyish brown (10YR 5/2).

Site RB

Elevation: 290m

Vegetation: Heather

Soil Type: Ironpan Stagnopodzol

Soil Survey of England and Wales description: Belmont association

Parent Material: Paleozoic and Pre-Cambic mudstones, slates and sandstones

Notes: Drainage at this site was good, as although the study area was flat the ground sloped steeply into a valley from about ten meters away.

Depth	Characteristics
	Litter layer of decomposing heather, 1cm thick.
0-10cm	Humified peat with many fine plant roots, colour; stoneless, black (5YR 2/1).
10-35cm	Slightly stoney sandy loam, clear boundary, colour; dark reddish brown 5YR (3/4).
35-50cm	Sandy silt loam, slightly stoney, colour; brown (7.5 YR 4/4).

Site SRG

Elevation: 300m

Vegetation: Woodland

Soil Type: Typical Brown Earth

Soil Survey of England and Wales description: Newport 4 association

Parent Material: Paleozoic and Pre-Cambic mudstones, slates and sandstones

Depth	Characteristics
	Litter layer of decomposing deciduous leaves, 0-4cm thick.
0-25cm	Slightly loamy medium sand, slightly stoney, colour; dark greyish brown (10YR 4/2), many fine roots.
25-50cm	Slightly stoney loamy medium sand, colour; brown (10YR 3/3) common fine roots.

Appendix 2

Metal Sensitivity

Metal	*Principal Line*	*Sensitivity mg/l*
Cadmium	228.8	0.01
Copper	324.8	0.04
Iron	248.3	0.06
Lead	217	0.1
Manganese	279.5	0.03
Nickel	232	0.06
Zinc	213.9	0.01

Appendix 3

Data Tables

The tables contain the data collected from the various extraction schemes and determinations. The soil physiochemical properties for a site are repeated with the data for each metal, to allow comparisons. All determinations were made with 6 replications.

Extraction Scheme	*Label*	*Meaning*
Sequential Extraction	Exchangeable	Sequential extraction fractions
Scheme	Carbonate	
	FMO	
	Organic	
	FeO	
	Residual	
	SUM	Sum of Sequential Extraction [HM]
Total Digestion	Digest	Total Digestion [HM]
	SUM%Digest	Sum of Sequential extraction fractions as % of total digestion [HM].
Organic Matter Extraction	HA	Humic Acid [HM]
	FA	Fulvic Acid [HM]
	HA g	Humic Acid yield
	FA G	Fulvic Acid yield
Physiochemical Properties	pH	
	LOI	Loss on Ignition 375°C
	LOIR	Loss on Ignition 375°C Repeat for site HA
	OC	Organic Carbon
	CEC	Cation Exchange Capacity
Parallel Extraction	PYR10FE	Pyrophosphate extractable iron pH10
	PYR7FE	Pyrophosphate extractable iron pH7
	PYR10	Pyrophosphate extractable metal pH10
	PYR7	Pyrophosphate extractable metal pH7
	NAOH	0.1M NaOH extn [hm]
	PEFA	Fulvic Acid [HM]
	PEHA	Humic Acid [HM]

HALLEN Site HA Lead

Profile	Exchange mg/kg	Carbonate mg/kg	FMO mg/kg	Organic mg/kg	Residual mg/kg	SUM mg/kg	Digest mg/kg	SUM%D %	HA mg/kg	FA mg/kg	LOI %
0-5cm	234.5	359.0	321.5	778.5	167.0	1860.5	2525	73.7	5.05	0.95	66.3
0-5cm	244.5	357.0	310.5	832.0	170.0	1914.0	2445	78.3	7.1	0.65	66
0-5cm	257.5	377.0	294.0	777.5	117.0	1823.0	2490	73.2	16.8	0.95	66.6
0-5cm	243.0	392.0	315.5	853.5	179.0	1983.0	2410	82.3	7.8	0.85	66.4
0-5cm	261.5	368.0	329.5	830.0	184.0	1973.0	2465	80.0	12	0.9	69.4
0-5cm	235.0	348.5	330.5	876.5	180.0	1970.5	2440	80.8	3.7	0.95	68.2
5-10cm	37.5	49.5	79.0	60.0	64.5	290.5	270	107.6	6.45	0.9	12.1
5-10cm	41.5	52.0	77.0	59.0	56.5	286.0	285	100.4	5.1	0.7	12.7
5-10cm	40.5	51.5	78.5	57.5	66.0	294.0	295	99.7	33.7	0.65	13.2
5-10cm	38.5	49.0	75.5	60.0	55.5	278.5	270	103.1	21.95	0.85	13
5-10cm	41.0	51.0	85.5	64.0	64.0	305.5	300	101.8	26.9	0.95	12.9
5-10cm	39.5	49.5	76.0	59.0	59.5	283.5	285	99.5	12	0.95	13
10-15cm	16.3	36.8	69.8	32.5	41.0	196.3	205	95.7	2.3	0.7	8.4
10-15cm	17.3	34.0	68.5	33.5	40.5	193.8	207	93.6	1.95	0.95	8.5
10-15cm	17.5	39.5	71.5	34.3	44.5	207.3	208	99.6	1.75	0.95	8.3
10-15cm	16.8	38.5	74.0	32.3	48.5	210.0	205	102.4	2.35	0.95	8.3
10-15cm	17.5	39.3	70.0	30.8	46.0	203.5	200	101.8	2.15	1.1	8.5
10-15cm	16.3	37.3	71.3	33.8	43.5	202.0	203	99.5	2.05	0.85	8.4
15-25cm	16.3	39.8	83.3	28.2	43.5	211.0	235	89.8	1.7	0.75	7.8
15-25cm	15.5	47.8	82.5	31.0	42.0	218.8	232	94.3	1.8	0.65	8.2
15-25cm	17.0	46.5	75.5	30.5	45.0	214.5	236	90.9	1.65	0.85	8.1
15-25cm	16.8	43.3	81.0	30.8	50.5	222.3	237	93.8	1.75	0.65	8
15-25cm	16.3	48.8	76.0	31.0	46.5	218.5	239	91.4	1.7	0.9	8
15-25cm		52.3	67.5	37.0	46.0	202.8	238	85.2	1.8	0.7	7.9
25-35cm	9.8	43.3	68.0	23.3	71.0	215.3	218	98.7	1.35	0.8	5.5
25-35cm		37.3	52.0	21.8	54.5	165.5	214	77.3	1.55	0.65	5.4
25-35cm	8.3	44.0	61.0	24.8	62.0	200.0	225	88.9	1.4	0.7	5.4
25-35cm	9.5	50.2	77.3	26.5	75.5	239.0	197	121.3	1.05	0.7	5.3
25-35cm	9.3	43.8	63.0	26.3	78.5	220.8	205	107.7	2.1	0.65	5.4
25-35cm	8.3	37.0	56.3	18.8	55.5	175.8	207	84.9	1.6	0.75	5.2
35-50cm	7.2	31.3	35.3	24.3	49.5	147.5	161	91.6	1.4	0.7	4.3
35-50cm	9.5	31.8	38.5	26.0	49.0	154.8	151	102.5	1.5	0.95	4.3
35-50cm	9.5	31.5	39.8	26.5	52.0	159.3	138	115.4	1.55	0.75	4.3
35-50cm	10.0	28.7	37.0	22.0	44.5	142.3	159	89.5	1.4	0.9	4.2
35-50cm	8.8	30.5	43.0	24.8	52.5	159.5	151	105.6	1.4	0.85	4.1
35-50cm	7.8	32.5	38.5	28.0	46.0	152.8	146	104.6	1.4	0.75	4.1

	HA g g	FA g g	pH	OC %	CEC me/100g	PYR7Fe mg/kg Fe	PYR7 mg/kg	NaOH mg/kg	PEFA mg/kg	LOIR %
0-5cm	0.0193	0.0295	5.1	35.9	34	1100	1751	467.5	372.5	66
0-5cm	0.1742	0.0322	5.1	35.4	34.5	1080	1727	475	377.5	65.7
0-5cm	0.0204	0.0247	5.0	37.4	34	1090	1730	457.5	397.5	66.3
0-5cm	0.1197	0.0298	5.1	37.7	35.5	1060	1727	477.5	395	66.1
0-5cm	0.0798	0.0307	5.1	36	36	1090	1760	455	402.5	69.2
0-5cm	0.0093	0.0258	5.1	36.7	34.5	1090	1744	455.5	374.75	68
5-10cm	0.0367	0.0238	5.5	6.3	26	1860	282	18.75	14	11.6
5-10cm	0.0202	0.0224	5.4	6.4	26.5	1670	267	13.5	11.75	12
5-10cm	0.0327	0.0225	5.5	5.9	25.5	1720	269	15.25	13.25	12.7
5-10cm	0.0458	0.0222	5.5	6.1	26.5	1670	262	14.25	12.75	12.5
5-10cm	0.0315	0.0235	5.4	6.1	26	1640	257	14.25	12.25	12.4
5-10cm	0.0405	0.0234	5.5	6.2	27.5	1620	274	17.25	13	12.5
10-15cm	0.0304	0.0189	6.5	5.5	18.5	1130	156	6.25	5	7.8
10-15cm	0.0166	0.0229	6.5	5.5	17.5	1130	154	6.5	5.25	7.8
10-15cm	0.0148	0.0168	6.5	5.5	16.5	1160	160	6.75	6.25	7.7
10-15cm	0.0184	0.0184	6.5	5.5	18	1150	167	7	5.25	7.8
10-15cm	0.0372	0.0193	6.5	5.6	17	1140	157	7.25	6	8
10-15cm	0.0360	0.0148	6.4	5.5	18	1160	163	5.75	4.5	7.8
15-25cm	0.0131		6.6	4.3	14.5	910	159	7	5	7.2
15-25cm	0.0140		6.5	4.3	12.5	920	157	6.75	5.25	7.5
15-25cm	0.0063		6.6	4.2	14.5	940	158	7.25	6.25	7.6
15-25cm	0.0143		6.6	4.4	14	950	160	6.75	5.25	7.4
15-25cm	0.0156		6.5	4.4	12.5	930	159	7	6	7.4
15-25cm	0.0112		6.6	4.4	15.5	940	158	6.75	4.5	15.6
25-35cm	0.0169	0.0205	7.0	2.6	4.5	590	111	3.25	3	5
25-35cm	0.0073	0.0216	7.0	2.6	6.5	610	119	3.25	3.25	4.9
25-35cm	0.0063	0.0161	7.0	2.7	6	570	113	4	3.5	4.9
25-35cm	0.0075	0.0225	7.0	2.6	4	580	112	4	3.25	4.9
25-35cm	0.0150	0.0156	7.1	2.6	9	620	110	4	3.5	4.9
25-35cm	0.0059	0.0228	7.0	2.6	3.5	610	113	4.25	3.25	4.8
35-50cm	0.0185	0.0152	7.1	2.5	1.5	620	92	3	2.5	3.8
35-50cm	0.0050	0.0156	7.2	2.6	2	640	94	3.5	2.75	3.9
35-50cm	0.0118	0.0179	7.2	2.5	2	630	94	4	2.5	3.8
35-50cm	0.0053	0.0160	7.1	2.6	2	630	96	4	3	3.7
35-50cm	0.0137	0.0162	7.1	2.5	1.5	620	92	4	3.75	3.6
35-50cm	0.0241	0.0157	7.1	2.5	3.5	630	94	3.75	2.25	3.6

HALLEN Site HA Zinc

Profile	Exchange mg/kg	Carbonate mg/kg	FMO mg/kg	Organic mg/kg	Residual mg/kg	SUM mg/kg	Digest mg/kg	SUM%D %	HA mg/kg	FA mg/kg	LOI %
0-5cm	464.5	490.0	488.5	518.0	259.5	2220.5	3715	59.8	6.5	0.65	66.3
0-5cm	454.0	469.0	463.0	520.0	275.5	2181.5	3410	64.0	5.9	0.55	66
0-5cm	485.5	484.5	486.5	502.5	240.5	2199.5	3580	61.4	6.9	0.55	66.6
0-5cm	446.5	509.5	478.5	522.0	308.5	2265.0	3505	64.6	6.3	0.5	66.4
0-5cm	474.5	497.5	507.5	520.0	309.0	2308.5	3595	64.2	5.75	0.45	69.4
0-5cm	418.0	491.0	487.0	532.5	328.0	2256.5	3735	60.4	6.75	0.65	68.2
5-10cm	398.0	273.0	480.0	123.0	263.5	1537.5	1665	92.3	10.85	0.7	12.1
5-10cm	438.5	273.5	469.0	130.5	266.5	1578.0	1675	94.2	6.3	0.5	12.7
5-10cm	398.0	282.5	508.5	121.0	284.5	1594.5	1640	97.2	11.7	0.5	13.2
5-10cm	399.0	293.5	496.5	124.0	254.0	1567.0	1660	94.4	10.05	0.7	13
5-10cm	453.5	307.0	502.0	117.0	247.5	1627.0	1655	98.3	5.15	0.45	12.9
5-10cm	413.0	294.0	492.0	124.5	264.0	1587.5	1765	89.9	9.8	0.55	13
10-15cm	20.8	110.3	217.5	20.3	162.0	530.8	500	106.2	6.45	0.55	8.4
10-15cm	20.5	101.8	222.3	23.3	167.0	534.8	503	106.3	17.55	0.55	8.5
10-15cm	20.0	114.0	218.0	22.5	166.0	540.5	547	98.8	15.2	0.45	8.3
10-15cm	21.8	107.0	217.0	21.5	166.5	533.8	490	108.9	12.15	0.6	8.3
10-15cm	22.5	113.0	209.2	20.0	175.0	539.8	513	105.2	7.2	0.6	8.5
10-15cm	22.8	105.5	202.8	21.3	165.5	517.8	535	96.8	9.4	0.45	8.4
15-25cm	13.8	80.3	201.3	17.5	152.5	465.3	457	101.8	4.15	0.5	7.8
15-25cm	13.3	88.0	200.3	19.0	156.0	476.5	456	104.5	3.75	0.45	8.2
15-25cm	14.5	90.8	185.3	20.5	160.0	471.0	454	103.7	3.9	0.55	8.1
15-25cm	13.3	87.3	192.3	18.0	149.5	460.3	469	98.1	3.9	0.5	8
15-25cm	14.0	95.5	196.5	18.8	190.0	514.8	466	110.5	4.1	0.5	8
15-25cm		104.3	154.5	28.2	166.5	453.5	462	98.2	4	0.55	7.9
25-35cm	2.8	35.0	72.0	7.5	114.5	231.8	254	91.2	1.8	0.55	5.5
25-35cm		34.3	65.3	7.8	121.0	228.3	250	91.3	3.45	0.6	5.4
25-35cm	4.0	35.3	66.0	7.8	117.5	230.5	256	90.0	1.9	0.55	5.4
25-35cm	3.5	34.3	68.8	6.5	108.5	221.5	237	93.5	3.2	0.55	5.3
25-35cm	3.0	33.3	65.0	7.2	117.5	226.0	248	91.1	3	0.55	5.4
25-35cm	2.5	34.8	70.0	7.5	115.5	230.3	245	94.0	3.85	0.55	5.2
35-50cm	2.3	15.5	25.5	3.5	86.5	133.3	142	93.8	2.9	0.45	4.3
35-50cm	2.0	14.2	25.5	3.5	85.0	130.3	141	92.4	1.5	0.5	4.3
35-50cm	2.3	14.2	24.8	3.8	90.0	135.0	136	99.3	2.5	0.45	4.3
35-50cm	2.3	15.0	26.5	3.8	90.0	137.5	141	97.5	3.2	0.5	4.2
35-50cm	2.5	15.3	26.0	3.8	90.5	138.0	139	99.3	2.3	0.55	4.1
35-50cm	2.5	15.0	24.8	3.8	88.5	134.5	135	99.6	2.25	0.5	4.1

	HA g g	FA g g	pH	OC %	CEC me/100g	PYR7Fe mg/kg Fe	PYR7 mg/kg	NaOH mg/kg	PEFA mg/kg	LOIR %
0-5cm	0.0193	0.0295	5.1	35.9	34	1100	2201	150.25	149.75	66
0-5cm	0.1742	0.0322	5.1	35.4	34.5	1080	2163	156.25	149.75	65.7
0-5cm	0.0204	0.0247	5.0	37.4	34	1090	2208	158.5	151	66.3
0-5cm	0.1197	0.0298	5.1	37.7	35.5	1060	2203	147.25	151.75	66.1
0-5cm	0.0798	0.0307	5.1	36	36	1090	2191	153.5	152.25	69.2
0-5cm	0.0093	0.0258	5.1	36.7	34.5	1090	2234	155.75	151	68
5-10cm	0.0367	0.0238	5.5	6.3	26	1860	1232	63.75	56	11.6
5-10cm	0.0202	0.0224	5.4	6.4	26.5	1670	1159	66.75	59.5	12
5-10cm	0.0327	0.0225	5.5	5.9	25.5	1720	1190	61	55.25	12.7
5-10cm	0.0458	0.0222	5.5	6.1	26.5	1670	1158	58.25	52.25	12.5
5-10cm	0.0315	0.0235	5.4	6.1	26	1640	1142	61.75	55.75	12.4
5-10cm	0.0405	0.0234	5.5	6.2	27.5	1620	1113	65.5	50.5	12.5
10-15cm	0.0304	0.0189	6.5	5.5	18.5	1130	328	10.5	6.5	7.8
10-15cm	0.0166	0.0229	6.5	5.5	17.5	1130	324	13.75	5.75	7.8
10-15cm	0.0148	0.0168	6.5	5.5	16.5	1160	330	14.25	6	7.7
10-15cm	0.0184	0.0184	6.5	5.5	18	1150	350	12	7.25	7.8
10-15cm	0.0372	0.0193	6.5	5.6	17	1140	334	15.25	6.75	8
10-15cm	0.0360	0.0148	6.4	5.5	18	1160	330	16.25	5.75	7.8
15-25cm	0.0131		6.6	4.3	14.5	910	281	8.75	6.5	7.2
15-25cm	0.0140		6.5	4.3	12.5	920	268	9.5	5.75	7.5
15-25cm	0.0063		6.6	4.2	14.5	940	277	10.25	6	7.6
15-25cm	0.0143		6.6	4.4	14	950	282	8	7.25	7.4
15-25cm	0.0156		6.5	4.4	12.5	930	271	7.75	6.75	7.4
15-25cm	0.0112		6.6	4.4	15.5	940	276	9.75	5.75	15.6
25-35cm	0.0169	0.0205	7.0	2.6	4.5	590	134	1.75	1.5	5
25-35cm	0.0073	0.0216	7.0	2.6	6.5	610	142	1.5	1.5	4.9
25-35cm	0.0063	0.0161	7.0	2.7	6	570	135	1.5	1.5	4.9
25-35cm	0.0075	0.0225	7.0	2.6	4	580	138	1.5	1.5	4.9
25-35cm	0.0150	0.0156	7.1	2.6	9	620	136	1.5	1.5	4.9
25-35cm	0.0059	0.0228	7.0	2.6	3.5	610	136	1.5	1.5	4.8
35-50cm	0.0185	0.0152	7.1	2.5	1.5	620	87	0.75	0.75	3.8
35-50cm	0.0050	0.0156	7.2	2.6	2	640	89	0.75	0.75	3.9
35-50cm	0.0118	0.0179	7.2	2.5	2	630	89	1	0.75	3.8
35-50cm	0.0053	0.0160	7.1	2.6	2	630	90	0.75	0.75	3.7
35-50cm	0.0137	0.0162	7.1	2.5	1.5	620	90	0.75	0.5	3.6
35-50cm	0.0241	0.0157	7.1	2.5	3.5	630	89	0.75	0.5	3.6

HALLEN Site HA Cadmium

Profile	Exchange mg/kg	Carbonate mg/kg	FMO mg/kg	Organic mg/kg	Residual mg/kg	SUM mg/kg	Digest mg/kg	SUM%D %	HA mg/kg	FA mg/kg	LOI %
0-5cm	8.7	11.2	5.0	5.4	1.4	31.6	36	89.0	0	0	66.3
0-5cm	8.0	11.6	5.5	5.8	1.8	32.5	36	91.5	0	0	66
0-5cm	10.0	10.7	4.7	5.3	2.0	32.7	39	84.8	0	0	66.6
0-5cm	8.7	11.6	5.5	6.0	1.8	33.5	38	88.2	0	0	66.4
0-5cm	9.8	10.2	5.1	5.8	1.7	32.5	38	86.7	0	0	69.4
0-5cm	8.1	11.4	5.8	6.0	1.9	33.1	40	83.7	0	0	68.2
5-10cm	10.3	3.6	1.8	1.1	1.6	18.2	20	93.3	0	0	12.1
5-10cm	13.1	3.6	1.6	1.1	1.7	20.9	23	92.9	0	0	12.7
5-10cm	10.7	3.5	1.7	1.2	1.7	18.7	22	87.0	0	0	13.2
5-10cm	10.7	3.8	1.9	1.4	1.9	19.6	21	93.1	0	0	13
5-10cm	11.0	3.8	1.8	1.3	2.0	19.8	23	88.0	0	0	12.9
5-10cm	10.9	3.8	1.9	1.4	1.8	19.7	23	85.4	0	0	13
10-15cm	3.0	2.4	1.2	0.5	1.1	8.2	10	85.4	0	0	8.4
10-15cm	3.4	2.1	1.1	0.5	1.3	8.3	9	88.7	0	0	8.5
10-15cm	3.4	2.2	1.2	0.6	1.3	8.7	10	85.9	0	0	8.3
10-15cm	3.4	2.2	1.3	0.7	1.5	9.0	11	82.0	0	0	8.3
10-15cm	3.5	2.2	1.4	0.6	1.4	9.1	11	82.3	0	0	8.5
10-15cm	3.5	2.3	1.3	0.7	1.5	9.2	10	90.6	0	0	8.4
15-25cm	3.3	2.0	1.1	0.5	1.6	8.5	6	141.7	0	0	7.8
15-25cm	3.2	2.2	1.1	0.6	1.3	8.2	6	134.0	0	0	8.2
15-25cm	3.3	2.1	1.0	0.6	1.4	8.3	6	131.3	0	0	8.1
15-25cm	3.3	2.1	1.2	0.7	1.7	9.0	7	135.6	0	0	8
15-25cm	3.4	2.2	1.2	0.7	1.7	9.1	7	133.8	0	0	8
15-25cm		2.4	1.0	0.7	1.5	5.5	7	84.6	0	0	7.9
25-35cm	1.1	1.8	0.7	0.2	1.7	5.4	6	91.5	0	0	5.5
25-35cm		1.7	0.6	0.2	1.7	4.2	6	71.2	0	0	5.4
25-35cm	1.1	1.8	0.7	0.2	1.6	5.4	6	89.6	0	0	5.4
25-35cm	1.1	1.8	0.7	0.2	1.5	5.3	5	98.1	0	0	5.3
25-35cm	1.2	1.8	0.7	0.3	1.7	5.6	6	94.9	0	0	5.4
25-35cm	1.2	1.9	0.8	0.3	1.7	5.7	6	100.0	0	0	5.2
35-50cm	0.8	1.6	0.4	0.2	1.4	4.4	4	105.4	0	0	4.3
35-50cm	0.8	1.6	0.4	0.2	1.5	4.5	4	111.9	0	0	4.3
35-50cm	0.9	1.6	0.4	0.2	1.3	4.3	5	94.4	0	0	4.3
35-50cm	0.8	1.6	0.4	0.2	1.3	4.3	5	92.9	0	0	4.2
35-50cm	0.9	1.6	0.4	0.2	1.2	4.3	5	88.5	0	0	4.1
35-50cm	0.9	1.6	0.5	0.3	1.4	4.6	4	107.0	0	0	4.1

	HA g g	FA g g	pH	OC %	CEC me/100g	PYR7Fe mg/kg Fe	PYR7 mg/kg	NaOH mg/kg	PEFA mg/kg	LOIR %
0-5cm	0.0193	0.0295	5.1	35.9	34	1100	40	12.5	10	66
0-5cm	0.1742	0.0322	5.1	35.4	34.5	1080	38	12.5	10	65.7
0-5cm	0.0204	0.0247	5.0	37.4	34	1090	40	12	10.25	66.3
0-5cm	0.1197	0.0298	5.1	37.7	35.5	1060	39	12.75	10.5	66.1
0-5cm	0.0798	0.0307	5.1	36	36	1090	40	12.25	10.5	69.2
0-5cm	0.0093	0.0258	5.1	36.7	34.5	1090	40	12.5	10	68
5-10cm	0.0367	0.0238	5.5	6.3	26	1860	31	8.25	5.75	11.6
5-10cm	0.0202	0.0224	5.4	6.4	26.5	1670	30	6.5	5.5	12
5-10cm	0.0327	0.0225	5.5	5.9	25.5	1720	31	6.25	5.5	12.7
5-10cm	0.0458	0.0222	5.5	6.1	26.5	1670	30	6	5.5	12.5
5-10cm	0.0315	0.0235	5.4	6.1	26	1640	29	6	5.25	12.4
5-10cm	0.0405	0.0234	5.5	6.2	27.5	1620	31	6.25	5.5	12.5
10-15cm	0.0304	0.0189	6.5	5.5	18.5	1130	15	1.25	1	7.8
10-15cm	0.0166	0.0229	6.5	5.5	17.5	1130	15	1.25	1	7.8
10-15cm	0.0148	0.0168	6.5	5.5	16.5	1160	15	1.25	1	7.7
10-15cm	0.0184	0.0184	6.5	5.5	18	1150	15	1.25	1	7.8
10-15cm	0.0372	0.0193	6.5	5.6	17	1140	15	1.25	1	8
10-15cm	0.0360	0.0148	6.4	5.5	18	1160	15	1.25	1	7.8
15-25cm	0.0131		6.6	4.3	14.5	910	15	1.25	1	7.2
15-25cm	0.0140		6.5	4.3	12.5	920	15	1.25	1	7.5
15-25cm	0.0063		6.6	4.2	14.5	940	15	1.25	1	7.6
15-25cm	0.0143		6.6	4.4	14	950	15	1.25	1	7.4
15-25cm	0.0156		6.5	4.4	12.5	930	15	1.25	1	7.4
15-25cm	0.0112		6.6	4.4	15.5	940	15	1.25	1	15.6
25-35cm	0.0169	0.0205	7.0	2.6	4.5	590	12	0.75	0.5	5
25-35cm	0.0073	0.0216	7.0	2.6	6.5	610	13	0.75	0.5	4.9
25-35cm	0.0063	0.0161	7.0	2.7	6	570	12	0.75	0.5	4.9
25-35cm	0.0075	0.0225	7.0	2.6	4	580	12	0.75	0.5	4.9
25-35cm	0.0150	0.0156	7.1	2.6	9	620	11	0.75	0.5	4.9
25-35cm	0.0059	0.0228	7.0	2.6	3.5	610	13	0.75	0.5	4.8
35-50cm	0.0185	0.0152	7.1	2.5	1.5	620	11	0.5	0.25	3.8
35-50cm	0.0050	0.0156	7.2	2.6	2	640	11	0.5	0.25	3.9
35-50cm	0.0118	0.0179	7.2	2.5	2	630	11	0.5	0.25	3.8
35-50cm	0.0053	0.0160	7.1	2.6	2	630	11	0.5	0.25	3.7
35-50cm	0.0137	0.0162	7.1	2.5	1.5	620	10	0.5	0.25	3.6
35-50cm	0.0241	0.0157	7.1	2.5	3.5	630	11	0.5	0.25	3.6

HALLEN Site HA Copper

Profile	Exchange mg/kg	Carbonate mg/kg	FMO mg/kg	Organic mg/kg	Residual mg/kg	SUM mg/kg	Digest mg/kg	SUM%D %	HA mg/kg	FA mg/kg	LOI %
0-5cm	6.7	6.0	3.9	129.5	23.5	169.5	295	57.6	5.45	1.55	66.3
0-5cm	7.2	5.6	4.3	139.4	24.4	180.7	290	62.3	4.4	1.8	66
0-5cm	6.9	6.1	4.5	132.7	21.7	171.8	293	58.7	7.85	2	66.6
0-5cm	7.1	6.7	4.7	144.9	27.7	191.1	284	67.3	4.9	2.35	66.4
0-5cm	7.8	6.0	4.7	141.4	28.2	188.1	296	63.5	6.25	1.75	69.4
0-5cm	8.7	6.3	5.4	147.2	27.7	195.2	300	65.2	4.1	2.1	68.2
5-10cm	3.2	3.5	3.2	9.2	29.0	48.0	52	93.1	6.1	1.55	12.1
5-10cm	3.1	3.9	3.2	9.6	30.4	50.1	50	100.2	5.4	1.5	12.7
5-10cm	3.2	4.0	3.7	9.1	30.9	50.9	51	100.7	12.05	1.45	13.2
5-10cm	4.0	4.4	3.7	9.8	28.2	50.0	60	84.0	12.55	1.45	13
5-10cm	3.9	4.6	4.1	9.9	28.2	50.5	58	87.1	10.95	1.5	12.9
5-10cm	4.3	4.9	4.1	10.3	30.7	54.1	58	93.3	10.6	1.5	13
10-15cm	2.2	2.8	2.1	3.1	29.3	39.4	39	100.1	3.95	1.25	8.4
10-15cm	2.3	2.6	2.3	3.4	29.6	40.2	40	101.5	4.25	3.35	8.5
10-15cm	2.5	2.9	2.3	3.5	30.0	41.1	42	97.0	3.4	1.35	8.3
10-15cm	2.4	2.8	2.5	3.2	30.2	41.1	38	108.0	4	2.1	8.3
10-15cm	2.6	2.9	2.5	3.3	30.6	41.9	39	106.2	3.5	2.3	8.5
10-15cm	2.6	3.0	2.4	3.5	30.7	42.1	44	95.6	4.05	2.85	8.4
15-25cm	2.2	2.8	2.6	2.9	31.2	41.6	42	99.8	3.2	0.95	7.8
15-25cm	2.2	3.0	2.6	3.2	32.6	43.6	42	104.2	3.45	1.05	8.2
15-25cm	2.6	3.1	2.6	2.9	32.0	43.2	43	99.9	3.6	1.05	8.1
15-25cm	2.7	3.2	2.8	3.5	32.0	44.1	42	104.0	3.45	1.05	8
15-25cm	2.5	3.2	2.8	3.3	32.0	43.7	44	98.6	3.8	1	8
15-25cm		4.0	2.8	3.7	32.0	42.5	44	96.2	3.6	1.1	7.9
25-35cm	1.4	2.5	2.2	1.4	25.6	33.1	37	90.2	2	1	5.5
25-35cm		2.7	2.2	1.6	27.4	33.8	37	91.4	2.5	1.2	5.4
25-35cm	1.9	3.1	2.2	1.8	26.2	35.2	38	93.2	2.05	1	5.4
25-35cm	2.0	3.1	2.3	1.9	25.4	34.6	38	91.4	2.55	0.7	5.3
25-35cm	1.6	3.0	2.4	1.9	26.9	35.7	39	92.5	2.05	1.15	5.4
25-35cm	1.5	3.2	2.8	2.2	27.0	36.6	38	96.0	2.25	1.05	5.2
35-50cm	1.3	3.6	2.4	1.2	26.0	34.5	39	87.4	2.45	0.95	4.3
35-50cm	1.5	3.4	2.4	1.3	24.0	32.7	38	87.1	1.8	1.9	4.3
35-50cm	1.5	3.5	2.7	1.5	27.4	36.5	38	97.3	2.5	1.05	4.3
35-50cm	1.8	3.6	2.7	1.6	26.2	35.8	40	90.7	2.5	1.95	4.2
35-50cm	2.0	3.9	2.7	1.8	27.2	37.6	39	96.8	1.95	1.1	4.1
35-50cm	2.0	3.7	2.7	2.0	25.6	35.9	39	92.7	1.75	1.1	4.1

	HA g g	FA g g	pH	OC %	CEC me/100g	PYR7Fe mg/kg Fe	PYR7 mg/kg	NaOH mg/kg	PEFA mg/kg	LOIR %
0-5cm	0.0193	0.0295	5.1	35.9	34	1100	78	86	57.5	66
0-5cm	0.1742	0.0322	5.1	35.4	34.5	1080	78	88	57	65.7
0-5cm	0.0204	0.0247	5.0	37.4	34	1090	78	86	58	66.3
0-5cm	0.1197	0.0298	5.1	37.7	35.5	1060	78	87.5	58	66.1
0-5cm	0.0798	0.0307	5.1	36	36	1090	78	83.5	58.75	69.2
0-5cm	0.0093	0.0258	5.1	36.7	34.5	1090	78	88.5	57.75	68
5-10cm	0.0367	0.0238	5.5	6.3	26	1860	29	21.5	16.5	11.6
5-10cm	0.0202	0.0224	5.4	6.4	26.5	1670	29	20	16	12
5-10cm	0.0327	0.0225	5.5	5.9	25.5	1720	30	20	16.5	12.7
5-10cm	0.0458	0.0222	5.5	6.1	26.5	1670	29	20.25	16.5	12.5
5-10cm	0.0315	0.0235	5.4	6.1	26	1640	29	20	16.5	12.4
5-10cm	0.0405	0.0234	5.5	6.2	27.5	1620	29	20.5	16.5	12.5
10-15cm	0.0304	0.0189	6.5	5.5	18.5	1130	26	13	10.5	7.8
10-15cm	0.0166	0.0229	6.5	5.5	17.5	1130	24	13.25	10.5	7.8
10-15cm	0.0148	0.0168	6.5	5.5	16.5	1160	24	13.25	10.75	7.7
10-15cm	0.0184	0.0184	6.5	5.5	18	1150	26	12.5	11	7.8
10-15cm	0.0372	0.0193	6.5	5.6	17	1140	25	13.5	10.75	8
10-15cm	0.0360	0.0148	6.4	5.5	18	1160	24	12.75	10.75	7.8
15-25cm	0.0131		6.6	4.3	14.5	910	25	12.5	10.5	7.2
15-25cm	0.0140		6.5	4.3	12.5	920	24	12.5	10.5	7.5
15-25cm	0.0063		6.6	4.2	14.5	940	26	12.75	10.75	7.6
15-25cm	0.0143		6.6	4.4	14	950	26	12.75	11	7.4
15-25cm	0.0156		6.5	4.4	12.5	930	24	13	10.75	7.4
15-25cm	0.0112		6.6	4.4	15.5	940	24	12.75	10.75	15.6
25-35cm	0.0169	0.0205	7.0	2.6	4.5	590	19	7	7	5
25-35cm	0.0073	0.0216	7.0	2.6	6.5	610	21	6.25	6.5	4.9
25-35cm	0.0063	0.0161	7.0	2.7	6	570	21	6.5	6.25	4.9
25-35cm	0.0075	0.0225	7.0	2.6	4	580	20	7	6.75	4.9
25-35cm	0.0150	0.0156	7.1	2.6	9	620	20	6.75	6.75	4.9
25-35cm	0.0059	0.0228	7.0	2.6	3.5	610	20	7.25	6.5	4.8
35-50cm	0.0185	0.0152	7.1	2.5	1.5	620	19	7.25	5.5	3.8
35-50cm	0.0050	0.0156	7.2	2.6	2	640	20	6.25	5.75	3.9
35-50cm	0.0118	0.0179	7.2	2.5	2	630	20	6.5	5.75	3.8
35-50cm	0.0053	0.0160	7.1	2.6	2	630	19	6.25	5.5	3.7
35-50cm	0.0137	0.0162	7.1	2.5	1.5	620	21	6.5	6.25	3.6
35-50cm	0.0241	0.0157	7.1	2.5	3.5	630	20	6.75	6	3.6

HALLEN Site HA Iron

Profile	Exchange mg/kg	Carbonate mg/kg	FMO mg/kg	Organic mg/kg	Residual mg/kg	SUM mg/kg	Digest mg/kg	SUM%D %	HA mg/kg	FA mg/kg	LOI %
0-5cm	18.0	10.0	253.5	1730.0	4630.0	6641.5	8515	78.0	0	0	66.3
0-5cm	18.5	8.0	251.0	1815.0	4895.0	6987.5	8540	81.8	0	0	66
0-5cm	18.5	10.5	257.5	1835.0	4515.0	6636.5	8595	77.2	0	0	66.6
0-5cm	19.5	11.0	243.0	1910.0	4925.0	7108.5	7520	94.5	0	0	66.4
0-5cm	20.5	8.0	259.0	1960.0	5235.0	7482.5	7565	98.9	0	0	69.4
0-5cm	19.5	9.0	253.0	2035.0	4990.0	7306.5	8190	89.2	0	0	68.2
5-10cm	7.0	14.5	1395.0	1270.0	19900.0	22586.5	27350	82.6	0	0	12.1
5-10cm	5.5	14.5	1445.0	1295.0	19870.0	22630.0	27050	83.7	0	0	12.7
5-10cm	7.5	15.0	1390.0	1225.0	20295.0	22932.5	27500	83.4	0	0	13.2
5-10cm	8.0	13.0	1445.0	1205.0	18535.0	21206.0	26250	80.8	0	0	13
5-10cm	8.0	15.0	1515.0	1220.0	18675.0	21433.0	28000	76.5	0	0	12.9
5-10cm	8.0	14.5	1510.0	1295.0	20220.0	23047.5	26250	87.8	0	0	13
10-15cm	5.0	12.8	1715.0	767.5	19715.0	22215.3	21160	105.0	0	0	8.4
10-15cm	5.5	10.3	1717.5	797.5	19805.0	22335.8	23290	95.9	0	0	8.5
10-15cm	5.5	6.8	1730.0	787.5	19655.0	22184.8	23680	93.7	0	0	8.3
10-15cm	6.3	10.8	1690.0	745.0	20210.0	22662.0	22460	100.9	0	0	8.3
10-15cm	6.5	5.3	1727.5	770.0	20405.0	22914.3	24350	94.1	0	0	8.5
10-15cm	5.8	10.8	1732.5	782.5	19900.0	22431.5	23310	96.2	0	0	8.4
15-25cm	0.0	0.0	1645.0	667.5	19410.0	21722.5	19870	109.3	0	0	7.8
15-25cm	0.0	0.0	1642.5	672.5	20100.0	22415.0	20080	111.6	0	0	8.2
15-25cm	0.0	0.0	1602.5	677.5	20050.0	22330.0	20570	108.6	0	0	8.1
15-25cm	0.0	0.0	1585.0	675.0	19535.0	21795.0	19330	112.8	0	0	8
15-25cm	0.0	0.0	1672.5	690.0	19770.0	22132.5	19940	111.0	0	0	8
15-25cm		0.0	1587.5	717.5	20105.0	22410.0	19300	116.1	0	0	7.9
25-35cm	0.0	0.0	1457.5	347.5	19705.0	21510.0	25260	85.2	0	0	5.5
25-35cm		0.0	1310.0	390.0	20110.0	21810.0	26770	81.5	0	0	5.4
25-35cm	0.0	0.0	1297.5	390.0	19825.0	21512.5	26670	80.7	0	0	5.4
25-35cm	0.0	0.0	1420.0	362.5	19465.0	21247.5	22850	93.0	0	0	5.3
25-35cm	0.0	0.0	1227.5	360.0	14985.0	16572.5	24720	67.0	0	0	5.4
25-35cm	0.0	0.0	1537.5	375.0	19810.0	21722.5	23510	92.4	0	0	5.2
35-50cm	0.0	0.0	1012.5	417.5	17715.0	19145.0	20880	91.7	0	0	4.3
35-50cm	0.0	0.0	977.5	415.0	17340.0	18732.5	20780	90.1	0	0	4.3
35-50cm	0.0	0.0	972.5	445.0	18705.0	20122.5	20620	97.6	0	0	4.3
35-50cm	0.0	0.0	1130.0	462.5	18250.0	19842.5	22360	88.7	0	0	4.2
35-50cm	0.0	0.0	1112.5	465.0	18410.0	19987.5	23010	86.9	0	0	4.1
35-50cm	0.0	0.0	920.0	475.0	17810.0	19205.0	21350	90.0	0	0	4.1

	HA g g	FA g g	pH	OC %	CEC me/100g	PYR7Fe mg/kg Fe	mg/kg	NaOH mg/kg	PEFA mg/kg	LOIR %
0-5cm	0.0193	0.0295	5.1	35.9	34	1100		450	255	66
0-5cm	0.1742	0.0322	5.1	35.4	34.5	1080		462.5	252.5	65.7
0-5cm	0.0204	0.0247	5.0	37.4	34	1090		467.5	262.5	66.3
0-5cm	0.1197	0.0298	5.1	37.7	35.5	1060		407.5	262.5	66.1
0-5cm	0.0798	0.0307	5.1	36	36	1090		430	260	69.2
0-5cm	0.0093	0.0258	5.1	36.7	34.5	1090		395	265	68
5-10cm	0.0367	0.0238	5.5	6.3	26	1860		985	135	11.6
5-10cm	0.0202	0.0224	5.4	6.4	26.5	1670		597.5	107.5	12
5-10cm	0.0327	0.0225	5.5	5.9	25.5	1720		532.5	107.5	12.7
5-10cm	0.0458	0.0222	5.5	6.1	26.5	1670		472.5	102.5	12.5
5-10cm	0.0315	0.0235	5.4	6.1	26	1640		485	100	12.4
5-10cm	0.0405	0.0234	5.5	6.2	27.5	1620		607.5	112.5	12.5
10-15cm	0.0304	0.0189	6.5	5.5	18.5	1130		327.5	20	7.8
10-15cm	0.0166	0.0229	6.5	5.5	17.5	1130		477.5	20	7.8
10-15cm	0.0148	0.0168	6.5	5.5	16.5	1160		495	20	7.7
10-15cm	0.0184	0.0184	6.5	5.5	18	1150		402.5	22.5	7.8
10-15cm	0.0372	0.0193	6.5	5.6	17	1140		552.5	20	8
10-15cm	0.0360	0.0148	6.4	5.5	18	1160		497.5	22.5	7.8
15-25cm	0.0131		6.6	4.3	14.5	910		315	20	7.2
15-25cm	0.0140		6.5	4.3	12.5	920		382.5	20	7.5
15-25cm	0.0063		6.6	4.2	14.5	940		415	20	7.6
15-25cm	0.0143		6.6	4.4	14	950		315	22.5	7.4
15-25cm	0.0156		6.5	4.4	12.5	930		297.5	20	7.4
15-25cm	0.0112		6.6	4.4	15.5	940		302.5	22.5	15.6
25-35cm	0.0169	0.0205	7.0	2.6	4.5	590		100	7.5	5
25-35cm	0.0073	0.0216	7.0	2.6	6.5	610		90	7.5	4.9
25-35cm	0.0063	0.0161	7.0	2.7	6	570		62.5	5	4.9
25-35cm	0.0075	0.0225	7.0	2.6	4	580		82.5	7.5	4.9
25-35cm	0.0150	0.0156	7.1	2.6	9	620		105	7.5	4.9
25-35cm	0.0059	0.0228	7.0	2.6	3.5	610		100	7.5	4.8
35-50cm	0.0185	0.0152	7.1	2.5	1.5	620		27.5	5	3.8
35-50cm	0.0050	0.0156	7.2	2.6	2	640		30	7.5	3.9
35-50cm	0.0118	0.0179	7.2	2.5	2	630		30	7.5	3.8
35-50cm	0.0053	0.0160	7.1	2.6	2	630		22.5	7.5	3.7
35-50cm	0.0137	0.0162	7.1	2.5	1.5	620		20	7.5	3.6
35-50cm	0.0241	0.0157	7.1	2.5	3.5	630		25	5	3.6

HALLEN Site HA Manganese

Profile	Exchange mg/kg	Carbonate mg/kg	FMO mg/kg	Organic mg/kg	Residual mg/kg	SUM mg/kg	Digest mg/kg	SUM%D %	HA mg/kg	FA mg/kg	LOI %
0-5cm	38.6	54.3	45.5	13.4	30.2	181.9	214	85.0	1.5	0.1	66.3
0-5cm	34.1	56.7	50.7	16.7	32.3	190.5	220	86.6	0.15	0.15	66
0-5cm	43.8	53.7	45.0	14.5	29.8	186.7	261	71.5	0.2	0.15	66.6
0-5cm	37.9	55.3	43.1	15.5	32.4	184.1	204	90.2	0.25	0.15	66.4
0-5cm	44.3	52.8	43.8	15.4	33.9	190.1	250	76.0	0.75	0.2	69.4
0-5cm	35.9	53.9	60.4	20.7	34.3	205.2	210	97.9	1.2	0.15	68.2
5-10cm	80.6	78.8	150.8	38.3	77.6	426.1	464	91.8	4.1	0.15	12.1
5-10cm	59.1	76.6	147.6	38.1	78.9	400.3	481	83.2	1.5	0.2	12.7
5-10cm	83.2	77.8	150.7	37.7	83.8	433.1	467	92.7	0.25	0.2	13.2
5-10cm	81.7	80.0	161.4	40.3	73.0	436.2	472	92.4	2.95	0.2	13
5-10cm	84.8	77.9	157.3	38.1	74.1	432.0	596	72.5	7	0.15	12.9
5-10cm	82.7	77.7	157.5	40.3	83.6	441.7	497	88.9	0.2	0.2	13
10-15cm	18.4	61.1	316.3	40.8	81.0	517.5	533	97.1	3.35	0.2	8.4
10-15cm	20.5	56.6	306.3	42.5	88.5	514.3	474	108.5	1.7	0.2	8.5
10-15cm	21.0	59.4	323.3	46.3	85.0	534.9	548	97.6	1.45	0.15	8.3
10-15cm	21.4	57.7	309.0	42.5	89.5	520.1	527	98.7	2.15	0.2	8.3
10-15cm	21.6	58.3	312.3	42.8	91.0	525.9	548	96.0	1.75	0.15	8.5
10-15cm	20.9	60.2	310.8	46.3	89.0	527.1	570	92.5	1.1	0.2	8.4
15-25cm	21.0	47.5	300.3	34.8	89.0	492.5	513	96.0	1.1	0.05	7.8
15-25cm	22.3	49.0	272.5	36.0	93.5	473.3	552	85.7	1.1	0.1	8.2
15-25cm	22.5	51.0	277.3	35.0	91.5	477.3	446	107.0	0.05	0.05	8.1
15-25cm	21.5	53.0	279.5	33.3	89.5	476.8	487	97.9	0.3	0.1	8
15-25cm	22.3	53.0	319.0	42.3	95.5	532.0	509	104.5	1.35	0.05	8
15-25cm		114.5	234.5	40.8	97.5	487.3	544	89.6	0.15	0.05	7.9
25-35cm	6.8	102.8	317.5	55.8	95.0	577.8	608	95.0	0.9	0.15	5.5
25-35cm		101.0	307.0	55.8	98.5	562.3	620	90.7	2.5	0.2	5.4
25-35cm	7.0	101.5	298.0	53.3	92.0	551.8	598	92.3	0.85	0.05	5.4
25-35cm	6.8	100.0	302.3	50.5	93.0	552.5	647	85.4	3.55	0.2	5.3
25-35cm	6.8	100.8	303.0	52.8	97.5	560.8	690	81.3	2	0.15	5.4
25-35cm	6.8	99.8	304.3	49.8	94.5	555.0	690	80.4	1.6	0.2	5.2
35-50cm	3.8	71.8	143.3	28.7	77.5	325.0	342	95.0	2.45	0.15	4.3
35-50cm	4.0	71.8	156.8	31.8	75.0	339.3	352	96.4	2	0.3	4.3
35-50cm	4.0	66.5	128.3	29.5	84.5	312.8	317	98.7	1.55	0.15	4.3
35-50cm	3.8	69.8	157.8	31.5	78.5	341.3	370	92.2	1.95	0.1	4.2
35-50cm	4.0	76.0	180.0	36.8	81.0	377.8	377	100.2	1.65	0.25	4.1
35-50cm	3.8	73.5	140.5	35.0	79.0	331.8	364	91.1	2.1	0.2	4.1

	HA g g	FA g g	pH	OC %	CEC me/100g	PYR7Fe mg/kg Fe	PYR7 mg/kg	NaOH mg/kg	PEFA mg/kg	LOIR %
0-5cm	0.0193	0.0295	5.1	35.9	34	1100				66
0-5cm	0.1742	0.0322	5.1	35.4	34.5	1080				65.7
0-5cm	0.0204	0.0247	5.0	37.4	34	1090				66.3
0-5cm	0.1197	0.0298	5.1	37.7	35.5	1060				66.1
0-5cm	0.0798	0.0307	5.1	36	36	1090				69.2
0-5cm	0.0093	0.0258	5.1	36.7	34.5	1090				68
5-10cm	0.0367	0.0238	5.5	6.3	26	1860				11.6
5-10cm	0.0202	0.0224	5.4	6.4	26.5	1670				12
5-10cm	0.0327	0.0225	5.5	5.9	25.5	1720				12.7
5-10cm	0.0458	0.0222	5.5	6.1	26.5	1670				12.5
5-10cm	0.0315	0.0235	5.4	6.1	26	1640				12.4
5-10cm	0.0405	0.0234	5.5	6.2	27.5	1620				12.5
10-15cm	0.0304	0.0189	6.5	5.5	18.5	1130				7.8
10-15cm	0.0166	0.0229	6.5	5.5	17.5	1130				7.8
10-15cm	0.0148	0.0168	6.5	5.5	16.5	1160				7.7
10-15cm	0.0184	0.0184	6.5	5.5	18	1150				7.8
10-15cm	0.0372	0.0193	6.5	5.6	17	1140				8
10-15cm	0.0360	0.0148	6.4	5.5	18	1160				7.8
15-25cm	0.0131		6.6	4.3	14.5	910				7.2
15-25cm	0.0140		6.5	4.3	12.5	920				7.5
15-25cm	0.0063		6.6	4.2	14.5	940				7.6
15-25cm	0.0143		6.6	4.4	14	950				7.4
15-25cm	0.0156		6.5	4.4	12.5	930				7.4
15-25cm	0.0112		6.6	4.4	15.5	940				15.6
25-35cm	0.0169	0.0205	7.0	2.6	4.5	590				5
25-35cm	0.0073	0.0216	7.0	2.6	6.5	610				4.9
25-35cm	0.0063	0.0161	7.0	2.7	6	570				4.9
25-35cm	0.0075	0.0225	7.0	2.6	4	580				4.9
25-35cm	0.0150	0.0156	7.1	2.6	9	620				4.9
25-35cm	0.0059	0.0228	7.0	2.6	3.5	610				4.8
35-50cm	0.0185	0.0152	7.1	2.5	1.5	620				3.8
35-50cm	0.0050	0.0156	7.2	2.6	2	640				3.9
35-50cm	0.0118	0.0179	7.2	2.5	2	630				3.8
35-50cm	0.0053	0.0160	7.1	2.6	2	630				3.7
35-50cm	0.0137	0.0162	7.1	2.5	1.5	620				3.6
35-50cm	0.0241	0.0157	7.1	2.5	3.5	630				3.6

RINGINGLOW Site RG Lead

Profile	Exchange mg/kg	Carbonate mg/kg	FMO mg/kg	Organic mg/kg	Residual mg/kg	SUM mg/kg	Digest mg/kg	SUM%D %	HA mg/kg	FA mg/kg	LOI %
0-5cm	8.3	17.0	56.5	59.5	93.0	234.3	208	112.4	1.45	0.45	20.32
0-5cm	8.8	19.0	59.0	59.8	96.0	242.5	224	108.3	1.6	0.5	19.95
0-5cm	9.3	19.5	59.8	62.5	88.0	239.0	213	112.2	1.25	0.625	20.87
0-5cm	10.8	20.0	59.0	64.0	93.5	247.3	225	109.7	1.8	0.55	19.47
0-5cm	11.5	20.3	60.8	62.3	85.5	240.3	216	111.1	1.55	0.375	22.28
0-5cm	12.8	19.5	59.8	63.2	87.0	242.3	201	120.7	1.2	0.625	21.86
5-10cm	11.5	18.8	56.5	35.8	46.1	168.6	179	94.1	1.5	0.575	12.59
5-10cm		20.5	52.5	37.0	48.5	158.5	182	87.3	1.45	0.75	13
5-10cm	14.8	19.0	54.3	36.8	44.6	169.4	177	95.9	1.05	0.475	13.09
5-10cm	13.3	20.3	56.8	35.5	48.9	174.6	180	96.9	1.45	0.675	12.88
5-10cm	14.8	19.5	55.3	37.3	48.6	175.3	190	92.2	1.6	0.475	12.99
5-10cm	15.8	21.5	57.5	36.8	49.6	181.1	175	103.2	1.7	0.675	12.92
10-15cm	12.6	24.5	46.3	23.6	38.4	145.4	156	93.1	0.1	0.5	10.36
10-15cm	12.2	26.9	43.9		58.4	141.3	155	90.9	0.15	0.575	10.24
10-15cm	11.8	25.4	43.4	24.2	42.0	146.8	170	86.5	0.2	0.45	10.46
10-15cm	12.9	29.8	48.3	24.1	41.9	156.9	162	96.9	0.05	0.4	10.28
10-15cm	12.7	26.8	44.3	22.6	43.3	149.5	161	92.8	0.25	0.55	10.39
10-15cm	12.8	28.7	46.3	26.5	68.2	182.4	167	109.3	0.15	0.5	10.5
15-25cm	13.4	15.9	26.3	15.9	31.1	102.5	103	99.0	0.2	0.5	8.06
15-25cm	14.2	16.7	23.5	15.1	27.7	97.3	106	91.5	0.2	0.575	8.1
15-25cm	13.3	17.3	28.7	16.1	32.8	108.3	106	102.0	0.25	0.55	8.23
15-25cm	13.5	18.7	27.6	17.1	36.0	112.9	105	107.2	0.25	0.55	8.03
15-25cm	13.6	18.6	27.5	17.4		77.0	109	70.5	0.25	0.525	7.95
15-25cm	14.0	18.7	28.7	17.8	35.1	114.3	111	103.1	0.25	0.55	8.08
25-35cm	12.1	15.9	12.7	9.2	28.2	78.1	79	98.8	0.1	0.1875	6.32
25-35cm	11.4	16.3	13.8	8.2	29.9	79.4	76	104.8	0.15	0.175	6.24
25-35cm	12.1	16.0	15.1	8.9	30.1	82.1	77	106.3	0.15	0.15	6.14
25-35cm	12.4	17.0	15.1	9.0	29.7	83.2	78	106.3	0.125	0.175	6.17
25-35cm	12.4	16.9	13.1	9.3	28.8	80.5	76	106.0	0.175	0.15	6.18
25-35cm	12.5	16.8	12.1	8.9	30.5	80.7	79	102.2	0.175	0.15	5.99
35-50cm	11.4	11.8	8.3	5.6	30.7	67.7	80	84.5	0.125	0.1375	5.22
35-50cm	11.7	12.4	7.5	5.4	31.7	68.8	73	94.1	0.1	0.1375	5.19
35-50cm	11.6	11.1	7.3	5.9	32.3	68.1	74	91.8	0.1	0.125	4.64
35-50cm	12.4	12.7	7.5	6.0	30.8	69.4	72	96.1	0.1	0.1375	4.67
35-50cm	12.4	12.9	7.1	6.6	30.3	69.3	74	94.2	0.1	0.1375	4.46
35-50cm	11.3	12.8	7.9	6.5	32.0	70.5	73	96.2	0.1	0.1375	4.64

	HA g g	FA g g	pH	OC %	CEC me/100g	PYR7Fe mg/kg Fe	PYR7 mg/kg	NaOH mg/kg	PEFA mg/kg
0-5cm	0.0264	0.0778	6.5	12.8	40.8	2300	143	12.5	9.5
0-5cm	0.0282	0.0717	6.5	12.1	41.6	2280	141	13.5	10
0-5cm	0.0254	0.0737	6.5	11.8	40	2280	140	13	12
0-5cm	0.0250	0.0738	6.6	13.8	40.5	2280	142	14	12.5
0-5cm	0.0272	0.0822	6.5	12.4	40.65	2340	144	14.5	12.5
0-5cm	0.0278	0.0764	6.4	13.3	38.9	2290	142	15	11.5
5-10cm	0.0220	0.0618	7.1	7.7	28.41	2290	135	9	6.5
5-10cm	0.0272	0.0674	7.2	7.6	28.62	2200	127	9.5	7.5
5-10cm	0.0230	0.0590	7.2	7.7	28.68	2200	130	10.5	7.5
5-10cm	0.0198	0.0617	7.2	7.3	28.62	2270	134	10.5	8.5
5-10cm	0.0238	0.0623	7.1	7.6	28.47	2310	133	9.5	9
5-10cm	0.0238	0.0662	7.2	7.5	28.5	2290	131	8.5	8
10-15cm	0.0174	0.2329	7.3	6.4	28.74	2120	116	4.75	3.5
10-15cm	0.0310	0.1542	7.3	6.3	28.77	2180	115	5.25	3.75
10-15cm	0.0238	0.0327	7.3	6.3	28.86	2170	116	5.75	4.5
10-15cm	0.0248	0.0220	7.3	6.2	28.8	2110	113	5.75	4.25
10-15cm	0.0298	0.1565	7.3	6.3	28.68	2150	114	5.5	4.5
10-15cm	0.0116	0.1765	7.2	6.3	28.77	2130	115	5.25	3.5
15-25cm	0.0194	0.1130	7.1	5.4	29.16	1700	93	4.25	4.75
15-25cm	0.0296	0.0279	7.2	5.4	29.04	1670	91	4.75	4.25
15-25cm	0.0332	0.0179	7.1	5.5	29.1	1700	95	4.5	4.75
15-25cm	0.0276	0.0343	7.2	5.4	29.07	1690	92	5.25	4.75
15-25cm	0.0258	0.0521	7.1	5.5	29.16	1700	94	4.75	5
15-25cm	0.0376	0.1065	7.1	5.3	29.16	1690	91	4.5	4
25-35cm	0.1012	0.0642	6.4	3.8	27.6	1380	79	5.25	3.75
25-35cm	0.1012	0.0692	6.3	3.7	27.66	1340	81	4.75	4.25
25-35cm	0.0860	0.6144	6.4	3.7	27.66	1330	80	5.5	4
25-35cm	0.0996	0.2426	6.4	3.7	27.63	1320	82	5.25	4
25-35cm	0.1048	0.1831	6.3	3.8	27.63	1350	79	6	4.5
25-35cm	0.0868	0.3711	6.4	3.7	27.6	1370	80	5.75	3.75
35-50cm	0.0472	0.0624	5.7	2.7	27.96	1130	76	6.75	5.75
35-50cm	0.0620	0.0537	5.7	2.9	27.81	1120	76	6.75	5.25
35-50cm	0.0384	0.0597	5.6	2.7	28.02	1100	75	7	5.5
35-50cm	0.0644	0.0611	5.7	2.7	28.14	1140	75	7.75	5.25
35-50cm	0.0632	0.0635	5.7	2.7	28.17	1140	76	7.75	5.75
35-50cm	0.0336	0.0527	5.7	2.7	27.45	1130	74	6.75	5.5

RINGINGLOW Site RG Zinc

Profile	Exchange mg/kg	Carbonate mg/kg	FMO mg/kg	Organic mg/kg	Residual mg/kg	SUM mg/kg	Digest mg/kg	SUM%D %	HA mg/kg	FA mg/kg	LOI %
0-5cm	2.2	5.5	21.2	14.7	43.0	86.5	85	101.8	0.35	0.375	20.32
0-5cm	2.2	5.1	21.1	16.6	41.5	86.4	89	97.4	0.55	0.325	19.95
0-5cm	2.1	5.1	20.8	14.4	40.0	82.4	85	97.3	0.4	0.35	20.87
0-5cm	2.1	5.0	22.1	15.7	40.6	85.4	86	98.9	0.45	0.375	19.47
0-5cm	2.3	5.7	21.2	14.6	41.5	85.2	85	100.0	0.35	0.325	22.28
0-5cm	2.1	5.0	21.5	14.8	41.5	84.8	82	103.4	0.65	0.375	21.86
5-10cm	1.6	2.3	13.3	9.1	45.2	71.6	70	101.8	0.35	0.325	12.59
5-10cm		2.4	13.4	8.7	43.3	67.7	71	95.2	0.5	0.325	13
5-10cm	1.4	2.2	13.5	9.1	45.2	71.3	73	97.4	2.4	0.325	13.09
5-10cm	1.3	2.2	13.6	8.7	45.1	70.8	68	104.7	1.9	0.35	12.88
5-10cm	1.7	2.2	13.5	8.7	45.6	71.6	71	101.5	0.8	0.325	12.99
5-10cm	1.4	2.2	13.4	9.0	47.0	72.9	73	100.5	1.35	0.325	12.92
10-15cm	1.6	2.2	10.7	6.2	37.2	57.8	59	97.9	0.7	0.35	10.36
10-15cm	1.3	2.2	10.0		42.1	55.6	58	95.5	2.7	0.325	10.24
10-15cm	1.4	2.2	10.2	6.9	37.8	58.5	69	85.1	0.5	0.325	10.46
10-15cm	2.2	2.2	10.7	6.1	38.2	59.3	62	96.5	1.15	0.325	10.28
10-15cm	1.3	2.4	10.6	6.3	37.1	57.6	61	94.7	1.55	0.325	10.39
10-15cm	1.5	2.3	10.8	6.2	38.2	58.9	60	97.6	1.2	0.35	10.5
15-25cm	1.5	1.9	8.0	4.7	31.2	47.3	48	99.1	0.4	0.325	8.06
15-25cm	1.3	1.9	7.6	4.4	29.6	44.8	47	95.3	1.2	0.325	8.1
15-25cm	1.3	1.8	8.3	4.6	31.8	47.8	47	100.8	1.7	0.45	8.23
15-25cm	2.6	2.0	8.1	4.7	31.5	48.9	45	108.1	0.95	0.425	8.03
15-25cm	12.6	2.0	8.1	4.4		27.0	48	56.5	2.2	0.225	7.95
15-25cm	1.4	1.8	10.1	5.1	32.8	51.1	46	111.6	0.9	0.375	8.08
25-35cm	2.2	2.3	5.4	3.2	26.4	39.5	37	106.3	0.275	0.225	6.32
25-35cm	2.3	2.5	6.1	2.9	26.9	40.6	37	108.8	0.75	0.1875	6.24
25-35cm	2.3	2.1	5.9	3.0	27.6	40.8	36	113.2	0.55	0.2	6.14
25-35cm	1.7	2.8	5.9	3.0	25.9	39.3	36	109.2	0.45	0.175	6.17
25-35cm	2.2	2.6	5.6	3.4	26.9	40.6	36	111.5	0.8	0.1875	6.18
25-35cm	2.1	2.3	6.1	2.9	27.1	40.4	36	112.5	0.525	0.2125	5.99
35-50cm	5.3	5.0	7.3	3.1	20.4	41.1	43	95.9	0.35	0.15	5.22
35-50cm	4.4	3.6	7.2	3.0	20.5	38.6	43	90.1	0.35	0.1875	5.19
35-50cm	3.6	5.6	6.3	2.8	20.5	38.7	42	92.1	0.35	0.325	4.64
35-50cm	4.1	3.6	6.7	3.1	19.9	37.3	42	89.8	0.325	0.3	4.67
35-50cm	3.6	4.6	7.4	2.8	20.5	38.8	43	91.4	0.4	0.1125	4.46
35-50cm	4.4	4.1	6.2	2.8	20.9	38.3	42	91.8	0.4	0.3625	4.64

	HA g g	FA g g	pH	OC %	CEC me/100g	PYR7Fe mg/kg Fe	PYR7 mg/kg
0-5cm	0.0264	0.0778	6.5	12.8	40.8	2300	79
0-5cm	0.0282	0.0717	6.5	12.1	41.6	2280	80
0-5cm	0.0254	0.0737	6.5	11.8	40	2280	80
0-5cm	0.0250	0.0738	6.6	13.8	40.5	2280	81
0-5cm	0.0272	0.0822	6.5	12.4	40.65	2340	80
0-5cm	0.0278	0.0764	6.4	13.3	38.9	2290	80
5-10cm	0.0220	0.0618	7.1	7.7	28.41	2290	66
5-10cm	0.0272	0.0674	7.2	7.6	28.62	2200	67
5-10cm	0.0230	0.0590	7.2	7.7	28.68	2200	67
5-10cm	0.0198	0.0617	7.2	7.3	28.62	2270	67
5-10cm	0.0238	0.0623	7.1	7.6	28.47	2310	66
5-10cm	0.0238	0.0662	7.2	7.5	28.5	2290	67
10-15cm	0.0174	0.2329	7.3	6.4	28.74	2120	62
10-15cm	0.0310	0.1542	7.3	6.3	28.77	2180	61
10-15cm	0.0238	0.0327	7.3	6.3	28.86	2170	63
10-15cm	0.0248	0.0220	7.3	6.2	28.8	2110	62
10-15cm	0.0298	0.1565	7.3	6.3	28.68	2150	64
10-15cm	0.0116	0.1765	7.2	6.3	28.77	2130	61
15-25cm	0.0194	0.1130	7.1	5.4	29.16	1700	64
15-25cm	0.0296	0.0279	7.2	5.4	29.04	1670	64
15-25cm	0.0332	0.0179	7.1	5.5	29.1	1700	64
15-25cm	0.0276	0.0343	7.2	5.4	29.07	1690	64
15-25cm	0.0258	0.0521	7.1	5.5	29.16	1700	64
15-25cm	0.0376	0.1065	7.1	5.3	29.16	1690	64
25-35cm	0.1012	0.0642	6.4	3.8	27.6	1380	65
25-35cm	0.1012	0.0692	6.3	3.7	27.66	1340	63
25-35cm	0.0860	0.6144	6.4	3.7	27.66	1330	63
25-35cm	0.0996	0.2426	6.4	3.7	27.63	1320	63
25-35cm	0.1048	0.1831	6.3	3.8	27.63	1350	64
25-35cm	0.0868	0.3711	6.4	3.7	27.6	1370	65
35-50cm	0.0472	0.0624	5.7	2.7	27.96	1130	62
35-50cm	0.0620	0.0537	5.7	2.9	27.81	1120	61
35-50cm	0.0384	0.0597	5.6	2.7	28.02	1100	62
35-50cm	0.0644	0.0611	5.7	2.7	28.14	1140	62
35-50cm	0.0632	0.0635	5.7	2.7	28.17	1140	62
35-50cm	0.0336	0.0527	5.7	2.7	27.45	1130	62

RINGINGLOW Site RG Copper

Profile	Exchange mg/kg	Carbonate mg/kg	FMO mg/kg	Organic mg/kg	Residual mg/kg	SUM mg/kg	Digest mg/kg	SUM%D %	HA mg/kg	FA mg/kg	LOI %
0-5cm	1.5	2.2	1.2	16.3	16.4	37.5	39	96.6	4.65	0.8	20.32
0-5cm	1.6	1.7	1.1	16.5	14.4	35.2	40	88.4	6.35	0.775	19.95
0-5cm	1.6	1.7	1.1	16.5	15.4	36.2	38	96.0	4.05	0.8	20.87
0-5cm	1.6	1.8	1.2	16.7	15.8	37.2	40	93.5	2.65	0.8	19.47
0-5cm	2.0	2.3	1.3	16.8	17.3	39.7	39	100.8	5.45	0.8	22.28
0-5cm	1.8	1.8	1.3	16.8	17.0	38.6	38	102.6	3.9	0.8	21.86
5-10cm	1.6	1.8	1.4	14.9	16.9	36.6	37	98.7	6.35	0.825	12.59
5-10cm		1.7	1.3	14.3	16.4	33.7	38	88.7	5.05	0.775	13
5-10cm	1.7	1.8	1.5	14.8	23.3	43.0	37	117.2	4.15	0.775	13.09
5-10cm	1.6	1.9	1.6	15.1	17.6	37.7	36	103.6	2.65	0.825	12.88
5-10cm	2.4	2.0	1.6	15.2	18.0	39.1	38	102.8	6	0.825	12.99
5-10cm	1.9	2.1	1.7	33.3	17.8	56.8	39	144.2	4.95	0.775	12.92
10-15cm	2.1	1.8	1.3	9.5	16.9	31.6	33	94.8	2.3	0.625	10.36
10-15cm	1.4	1.8	1.4		19.0	23.5	33	72.2	2.8	0.65	10.24
10-15cm	1.6	1.8	1.8	9.6	16.9	31.6	32	99.6	2.2	0.625	10.46
10-15cm	2.0	1.8	1.5	9.7	17.2	32.1	34	93.3	2.85	0.65	10.28
10-15cm	1.6	1.9	1.7	9.5	17.9	32.6	34	95.5	2.6	0.65	10.39
10-15cm	1.8	2.1	1.6	9.5	18.0	32.9	35	95.4	2.5	0.625	10.5
15-25cm	1.3	1.5	1.5	7.0	18.6	29.9	29	103.9	3.15	0.55	8.06
15-25cm	1.5	1.7	1.3	6.8	15.5	26.8	28	95.0	3.4	0.575	8.1
15-25cm	1.5	1.6	1.8	7.0	17.4	29.3	29	100.9	2.95	0.675	8.23
15-25cm	1.6	1.7	1.8	7.0	16.8	28.8	28	103.5	3.1	0.55	8.03
15-25cm	1.5	1.9	1.7	7.3		12.5	28	44.8	3.25	0.7	7.95
15-25cm	1.8	1.8	2.1	8.3	17.4	31.4	29	106.7	3.2	0.575	8.08
25-35cm	1.6	1.5	0.9	6.1	17.5	27.5	29	96.2	0.9	0.25	6.32
25-35cm	1.5	1.5	0.9	5.8	18.6	28.3	29	97.9	1.2	0.2875	6.24
25-35cm	1.6	1.6	0.9	5.8	19.0	28.8	28	102.2	1.175	0.2625	6.14
25-35cm	1.4	1.7	1.0	5.9	18.0	27.9	28	98.0	0.925	0.2625	6.17
25-35cm	1.5	1.6	1.1	6.8	18.7	29.6	29	103.3	0.875	0.25	6.18
25-35cm	1.5	1.6	1.1	6.3	18.2	28.7	28	102.5	0.95	0.275	5.99
35-50cm	2.3	2.4	1.6	8.4	18.7	33.4	31	108.4	1.075	0.25	5.22
35-50cm	2.1	1.8	2.1	8.5	19.3	33.8	31	109.2	1.225	0.35	5.19
35-50cm	1.8	2.3	1.6	8.2	18.3	32.2	29	111.6	0.95	0.65	4.64
35-50cm	2.0	2.1	1.7	8.6	17.9	32.2	29	110.1	1.1	0.6125	4.67
35-50cm	1.9	2.5	1.7	8.5	17.9	32.4	29	110.3	1.125	0.5125	4.46
35-50cm	2.0	2.3	1.6	8.4	18.3	32.6	29	111.9	1.15	0.35	4.64

	HA g g	FA g g	pH	OC %	CEC me/100g	PYR7Fe mg/kg Fe	PYR7 mg/kg	NaOH mg/kg	PEFA mg/kg
0-5cm	0.0264	0.0778	6.5	12.8	40.8	2300	24	15.5	11
0-5cm	0.0282	0.0717	6.5	12.1	41.6	2280	26	15.5	12
0-5cm	0.0254	0.0737	6.5	11.8	40	2280	26	15	11.5
0-5cm	0.0250	0.0738	6.6	13.8	40.5	2280	29	15	11.5
0-5cm	0.0272	0.0822	6.5	12.4	40.65	2340	25	14.5	11
0-5cm	0.0278	0.0764	6.4	13.3	38.9	2290	27	15	11.5
5-10cm	0.0220	0.0618	7.1	7.7	28.41	2290	25	11	10
5-10cm	0.0272	0.0674	7.2	7.6	28.62	2200	25	10.5	11
5-10cm	0.0230	0.0590	7.2	7.7	28.68	2200	26	10.5	10.5
5-10cm	0.0198	0.0617	7.2	7.3	28.62	2270	28	10.5	11
5-10cm	0.0238	0.0623	7.1	7.6	28.47	2310	28	11	10.5
5-10cm	0.0238	0.0662	7.2	7.5	28.5	2290	26	10.5	11
10-15cm	0.0174	0.2329	7.3	6.4	28.74	2120	22	7.25	7.5
10-15cm	0.0310	0.1542	7.3	6.3	28.77	2180	21	7.25	6
10-15cm	0.0238	0.0327	7.3	6.3	28.86	2170	23	7.25	6.75
10-15cm	0.0248	0.0220	7.3	6.2	28.8	2110	23	7.5	6
10-15cm	0.0298	0.1565	7.3	6.3	28.68	2150	22	7	6.75
10-15cm	0.0116	0.1765	7.2	6.3	28.77	2130	22	7.25	7.75
15-25cm	0.0194	0.1130	7.1	5.4	29.16	1700	19	6.5	5.5
15-25cm	0.0296	0.0279	7.2	5.4	29.04	1670	20	5.75	5.25
15-25cm	0.0332	0.0179	7.1	5.5	29.1	1700	20	5.75	4.75
15-25cm	0.0276	0.0343	7.2	5.4	29.07	1690	20	6	6.25
15-25cm	0.0258	0.0521	7.1	5.5	29.16	1700	20	6	7.5
15-25cm	0.0376	0.1065	7.1	5.3	29.16	1690	19	6.25	5
25-35cm	0.1012	0.0642	6.4	3.8	27.6	1380	20	6.25	5.5
25-35cm	0.1012	0.0692	6.3	3.7	27.66	1340	18	6.25	5.5
25-35cm	0.0860	0.6144	6.4	3.7	27.66	1330	18	6.25	5.25
25-35cm	0.0996	0.2426	6.4	3.7	27.63	1320	17	6.75	5.5
25-35cm	0.1048	0.1831	6.3	3.8	27.63	1350	18	6	5.25
25-35cm	0.0868	0.3711	6.4	3.7	27.6	1370	18	6.25	5.25
35-50cm	0.0472	0.0624	5.7	2.7	27.96	1130	18	9	6.25
35-50cm	0.0620	0.0537	5.7	2.9	27.81	1120	18	8.75	6.5
35-50cm	0.0384	0.0597	5.6	2.7	28.02	1100	18	9	6.75
35-50cm	0.0644	0.0611	5.7	2.7	28.14	1140	18	9	7
35-50cm	0.0632	0.0635	5.7	2.7	28.17	1140	19	9.25	7
35-50cm	0.0336	0.0527	5.7	2.7	27.45	1130	18	9	7

RINGINGLOW Site RG Nickel

Profile	Exchange mg/kg	Carbonate mg/kg	FMO mg/kg	Organic mg/kg	Residual mg/kg	SUM mg/kg	Digest mg/kg	SUM%D %	HA mg/kg	FA mg/kg	LOI %
0-5cm	6.1	6.0	3.1	4.7	18.8	38.6	38	102.8	0.5	0.65	20.32
0-5cm	5.8	5.6	3.2	4.8	13.5	32.9	34	97.3	0.9	0.525	19.95
0-5cm	5.6	6.2	3.3	4.8	14.8	34.7	33	106.0	0.45	0.8	20.87
0-5cm	5.2	6.7	3.7	4.9	14.3	34.7	44	78.6	0.55	0.85	19.47
0-5cm	6.0	5.9	4.0	5.0	19.0	39.8	36	110.9	0.25	0.5	22.28
0-5cm	6.1	6.8	3.2	4.9	19.7	40.6	45	90.7	0.75	0.65	21.86
5-10cm	5.1	4.8	3.1	3.2	16.1	32.3	30	106.4	1.05	0.6	12.59
5-10cm		4.2	2.8	2.8	19.7	29.5	28	105.6	0.5	0.575	13
5-10cm	4.8	4.8	3.1	2.8	15.1	30.4	44	69.6	0.65	0.75	13.09
5-10cm	4.8	4.2	3.1	3.1	20.7	35.8	38	93.7	0.8	0.675	12.88
5-10cm	4.7	4.5	2.9	3.2	16.7	31.9	42	75.3	0.3	0.55	12.99
5-10cm	4.6	4.5	2.7	3.3	17.4	32.5	41	79.1	0.75	0.425	12.92
10-15cm	4.9	5.8	2.5	2.0	24.0	39.2	44	88.2	0.3	0.7	10.36
10-15cm	5.0	6.1	2.5		24.6	38.2	44	87.4	0.45	0.5	10.24
10-15cm	4.4	6.5	2.6	1.9	19.9	35.3	44	80.3	0.65	0.8	10.46
10-15cm	5.0	6.2	2.7	2.2	31.1	47.2	45	105.8	0.45	0.775	10.28
10-15cm	5.0	6.3	2.8	2.2	23.3	39.5	49	81.1	0.3	0.625	10.39
10-15cm	5.0	6.5	2.7	1.9	16.5	32.6	39	83.3	0.35	0.875	10.5
15-25cm	5.0	5.6	1.9	1.6	74.8	89.0	65	136.9	0.45	0.7	8.06
15-25cm	5.7	5.4	1.6	1.7	36.8	51.1	61	83.4	0.5	0.525	8.1
15-25cm	5.1	5.8	2.1	1.3	25.0	39.3	46	85.8	0.45	0.55	8.23
15-25cm	5.1	5.7	1.9	1.8	24.2	38.6	48	80.1	0.45	0.625	8.03
15-25cm	5.3	5.9	1.8	2.3		15.3	52	29.2	0.5	0.6	7.95
15-25cm	5.1	5.6	1.7	1.5	37.2	51.0	51	100.8	0.5	0.65	8.08
25-35cm	5.8	4.9	14.2	5.2	15.3	45.4	42	107.2	0.175	0.1625	6.32
25-35cm	5.1	4.6	11.6	6.8	17.2	45.2	41	109.2	0.45	0.2375	6.24
25-35cm	4.7	4.9	10.6	6.2	17.5	43.9	49	89.7	0.225	0.2	6.14
25-35cm	4.8	5.1	12.5	8.1	18.3	48.8	45	109.1	0.425	0.2125	6.17
25-35cm	4.4	4.4	8.1	8.8	21.3	46.9	41	113.7	0.375	0.2	6.18
25-35cm	5.4	4.7	6.2	6.0	18.9	41.1	44	92.6	0.525	0.1625	5.99
35-50cm	5.5	5.4	3.2	1.7	11.4	27.1	37	73.7	0.2	0.4	5.22
35-50cm	5.5	4.8	3.3	2.2	11.3	27.1	38	71.4	0.225	0.2875	5.19
35-50cm	5.5	5.4	10.1	3.2	17.0	41.2	34	119.8	0.2	0.3	4.64
35-50cm	5.3	5.1	11.8	3.2	13.3	38.7	39	100.4	0.225	0.25	4.67
35-50cm	5.1	5.7	6.6	3.2	20.3	40.9	35	116.5	0.2	0.275	4.46
35-50cm	4.9	5.4	11.7	3.8	12.4	38.1	36	106.4	0.2	0.3375	4.64

	HA g g	FA g g	pH	OC %	CEC me/100g	PYR7Fe mg/kg Fe
0-5cm	0.0264	0.0778	6.5	12.8	40.8	2300
0-5cm	0.0282	0.0717	6.5	12.1	41.6	2280
0-5cm	0.0254	0.0737	6.5	11.8	40	2280
0-5cm	0.0250	0.0738	6.6	13.8	40.5	2280
0-5cm	0.0272	0.0822	6.5	12.4	40.65	2340
0-5cm	0.0278	0.0764	6.4	13.3	38.9	2290
5-10cm	0.0220	0.0618	7.1	7.7	28.41	2290
5-10cm	0.0272	0.0674	7.2	7.6	28.62	2200
5-10cm	0.0230	0.0590	7.2	7.7	28.68	2200
5-10cm	0.0198	0.0617	7.2	7.3	28.62	2270
5-10cm	0.0238	0.0623	7.1	7.6	28.47	2310
5-10cm	0.0238	0.0662	7.2	7.5	28.5	2290
10-15cm	0.0174	0.2329	7.3	6.4	28.74	2120
10-15cm	0.0310	0.1542	7.3	6.3	28.77	2180
10-15cm	0.0238	0.0327	7.3	6.3	28.86	2170
10-15cm	0.0248	0.0220	7.3	6.2	28.8	2110
10-15cm	0.0298	0.1565	7.3	6.3	28.68	2150
10-15cm	0.0116	0.1765	7.2	6.3	28.77	2130
15-25cm	0.0194	0.1130	7.1	5.4	29.16	1700
15-25cm	0.0296	0.0279	7.2	5.4	29.04	1670
15-25cm	0.0332	0.0179	7.1	5.5	29.1	1700
15-25cm	0.0276	0.0343	7.2	5.4	29.07	1690
15-25cm	0.0258	0.0521	7.1	5.5	29.16	1700
15-25cm	0.0376	0.1065	7.1	5.3	29.16	1690
25-35cm	0.1012	0.0642	6.4	3.8	27.6	1380
25-35cm	0.1012	0.0692	6.3	3.7	27.66	1340
25-35cm	0.0860	0.6144	6.4	3.7	27.66	1330
25-35cm	0.0996	0.2426	6.4	3.7	27.63	1320
25-35cm	0.1048	0.1831	6.3	3.8	27.63	1350
25-35cm	0.0868	0.3711	6.4	3.7	27.6	1370
35-50cm	0.0472	0.0624	5.7	2.7	27.96	1130
35-50cm	0.0620	0.0537	5.7	2.9	27.81	1120
35-50cm	0.0384	0.0597	5.6	2.7	28.02	1100
35-50cm	0.0644	0.0611	5.7	2.7	28.14	1140
35-50cm	0.0632	0.0635	5.7	2.7	28.17	1140
35-50cm	0.0336	0.0527	5.7	2.7	27.45	1130

RINGINGLOW Site RG Iron

Profile	Exchange mg/kg	Carbonate mg/kg	FMO mg/kg	Organic mg/kg	Residual mg/kg	SUM mg/kg	Digest mg/kg	SUM%D %	HA mg/kg	FA mg/kg	LOI %
0-5cm	0.0	0.0	2380.0	3155.0	12870.0	18405.0	18045	102.0	0	0	20.32
0-5cm	0.0	0.0	2362.5	3125.0	11925.0	17412.5	18765	92.8	0	0	19.95
0-5cm	0.0	0.0	2387.5	3127.5	11915.0	17430.0	18085	96.4	0	0	20.87
0-5cm	0.0	0.0	2340.0	3117.5	12430.0	17887.5	18255	98.0	0	0	19.47
0-5cm	0.0	0.0	2355.0	3292.5	12945.0	18592.5	17990	103.3	0	0	22.28
0-5cm	0.0	0.0	2425.0	3287.5	13090.0	18802.5	17485	107.5	0	0	21.86
5-10cm	0.0	0.0	3042.5	2262.5	15935.0	21240.0	20340	104.4	0	0	12.59
5-10cm		0.0	3140.0	2245.0	14905.0	20290.0	21220	95.6	0	0	13
5-10cm	0.0	0.0	3065.0	2267.5	16220.0	21552.5	19990	107.8	0	0	13.09
5-10cm	0.0	0.0	3147.5	2330.0	16675.0	22152.5	20085	110.3	0	0	12.88
5-10cm	0.0	0.0	3167.5	2375.0	16830.0	22372.5	20965	106.7	0	0	12.99
5-10cm	0.0	0.0	3152.5	2367.5	16740.0	22260.0	20865	106.7	0	0	12.92
10-15cm	0.0	0.0	3205.0	1542.5	20010.0	24757.5	26095	94.9	0	0	10.36
10-15cm	0.0	0.0	2897.5		21810.0	24707.5	26020	95.0	0	0	10.24
10-15cm	0.0	0.0	3087.5	1630.0	21130.0	25847.5	25755	100.4	0	0	10.46
10-15cm	0.0	0.0	3402.5	1577.5	21340.0	26320.0	27455	95.9	0	0	10.28
10-15cm	0.0	0.0	3290.0	1615.0	21515.0	26420.0	27560	95.9	0	0	10.39
10-15cm	0.0	0.0	3352.5	1610.0	21715.0	26677.5	27025	98.7	0	0	10.5
15-25cm	0.0	0.0	3087.5	1150.0	20745.0	24982.5	27820	89.8	0	0	8.06
15-25cm	0.0	0.0	2620.0	1095.0	20890.0	24605.0	26985	91.2	0	0	8.1
15-25cm	0.0	0.0	3212.5	1162.5	22640.0	27015.0	27640	97.7	0	0	8.23
15-25cm	0.0	0.0	2855.0	1267.5	22300.0	26422.5	26515	99.7	0	0	8.03
15-25cm	0.0	0.0	2790.0	1235.0		4025.0	26665	15.1	0	0	7.95
15-25cm	0.0	0.0	3160.0	1305.0	23485.0	27950.0	27010	103.5	0	0	8.08
25-35cm	0.0	0.0	2417.5	885.0	22885.0	26187.5	29070	90.1	0	0	6.32
25-35cm	0.0	0.0	2937.5	860.0	24225.0	28022.5	28865	97.1	0	0	6.24
25-35cm	0.0	0.0	2827.5	885.0	25320.0	29032.5	26715	108.7	0	0	6.14
25-35cm	0.0	0.0	3202.5	950.0	22440.0	26592.5	28015	94.9	0	0	6.17
25-35cm	0.0	0.0	2880.0	970.0	23800.0	27650.0	29185	94.7	0	0	6.18
25-35cm	0.0	0.0	2845.0	1067.5	23760.0	27672.5	28305	97.8	0	0	5.99
35-50cm	0.0	0.0	2435.0	722.5	16175.0	19332.5	20325	95.1	0	0	5.22
35-50cm	0.0	0.0	2502.5	735.0	16400.0	19637.5	20250	97.0	0	0	5.19
35-50cm	0.0	0.0	2260.0	780.0	16980.0	20020.0	18845	106.2	0	0	4.64
35-50cm	0.0	0.0	2402.5	822.5	16400.0	19625.0	19895	98.6	0	0	4.67
35-50cm	0.0	0.0	2437.5	740.0	15425.0	18602.5	20045	92.8	0	0	4.46
35-50cm	0.0	0.0	2685.0	762.5	16795.0	20242.5	19495	103.8	0	0	4.64

	HA g g	FA g g	pH	OC %	CEC me/100g	PYR7Fe mg/kg Fe	PYR7 mg/kg	NaOH mg/kg	PEFA mg/kg
0-5cm	0.0264	0.0778	6.5	12.8	40.8	2300		335	150
0-5cm	0.0282	0.0717	6.5	12.1	41.6	2280		355	160
0-5cm	0.0254	0.0737	6.5	11.8	40	2280		370	170
0-5cm	0.0250	0.0738	6.6	13.8	40.5	2280		370	175
0-5cm	0.0272	0.0822	6.5	12.4	40.65	2340		350	175
0-5cm	0.0278	0.0764	6.4	13.3	38.9	2290		360	170
5-10cm	0.0220	0.0618	7.1	7.7	28.41	2290		230	65
5-10cm	0.0272	0.0674	7.2	7.6	28.62	2200		225	70
5-10cm	0.0230	0.0590	7.2	7.7	28.68	2200		220	80
5-10cm	0.0198	0.0617	7.2	7.3	28.62	2270		245	90
5-10cm	0.0238	0.0623	7.1	7.6	28.47	2310		225	115
5-10cm	0.0238	0.0662	7.2	7.5	28.5	2290		230	50
10-15cm	0.0174	0.2329	7.3	6.4	28.74	2120		380	57.5
10-15cm	0.0310	0.1542	7.3	6.3	28.77	2180		380	45
10-15cm	0.0238	0.0327	7.3	6.3	28.86	2170		470	60
10-15cm	0.0248	0.0220	7.3	6.2	28.8	2110		465	55
10-15cm	0.0298	0.1565	7.3	6.3	28.68	2150		492.5	65
10-15cm	0.0116	0.1765	7.2	6.3	28.77	2130		395	57.5
15-25cm	0.0194	0.1130	7.1	5.4	29.16	1700		425	60
15-25cm	0.0296	0.0279	7.2	5.4	29.04	1670		407.5	72.5
15-25cm	0.0332	0.0179	7.1	5.5	29.1	1700		452.5	67.5
15-25cm	0.0276	0.0343	7.2	5.4	29.07	1690		587.5	70
15-25cm	0.0258	0.0521	7.1	5.5	29.16	1700		560	80
15-25cm	0.0376	0.1065	7.1	5.3	29.16	1690		400	72.5
25-35cm	0.1012	0.0642	6.4	3.8	27.6	1380		515	77.5
25-35cm	0.1012	0.0692	6.3	3.7	27.66	1340		497.5	82.5
25-35cm	0.0860	0.6144	6.4	3.7	27.66	1330		535	100
25-35cm	0.0996	0.2426	6.4	3.7	27.63	1320		495	90
25-35cm	0.1048	0.1831	6.3	3.8	27.63	1350		540	70
25-35cm	0.0868	0.3711	6.4	3.7	27.6	1370		500	87.5
35-50cm	0.0472	0.0624	5.7	2.7	27.96	1130		580	115
35-50cm	0.0620	0.0537	5.7	2.9	27.81	1120		572.5	75
35-50cm	0.0384	0.0597	5.6	2.7	28.02	1100		595	90
35-50cm	0.0644	0.0611	5.7	2.7	28.14	1140		590	82.5
35-50cm	0.0632	0.0635	5.7	2.7	28.17	1140		610	132.5
35-50cm	0.0336	0.0527	5.7	2.7	27.45	1130		605	130

RINGINGLOW Site RG Manganese

Profile	Exchange mg/kg	Carbonate mg/kg	FMO mg/kg	Organic mg/kg	Residual mg/kg	SUM mg/kg	Digest mg/kg	SUM%D %	HA mg/kg	FA mg/kg	LOI %
0-5cm	23.1	26.4	43.8	13.6	28.9	135.7	136	99.8	0	0	20.32
0-5cm	23.8	25.3	49.8	14.6	27.3	140.7	139	101.4	0	0	19.95
0-5cm	25.6	25.2	43.8	13.3	27.0	134.8	128	105.6	0	0	20.87
0-5cm	22.4	24.9	44.3	14.1	27.9	133.6	133	100.1	0	0	19.47
0-5cm	20.3	29.1	47.1	13.7	29.1	139.2	133	104.6	0	0	22.28
0-5cm	23.9	25.8	59.0	15.9	28.4	153.0	127	120.7	0	0	21.86
5-10cm	8.5	26.8	44.1	9.8	38.8	128.0	118	108.9	0	0	12.59
5-10cm		25.1	44.4	9.6	36.6	115.7	120	96.8	0	0	13
5-10cm	8.4	24.9	50.1	10.2	37.7	131.2	109	120.0	0	0	13.09
5-10cm	8.7	24.2	44.0	9.1	37.3	123.2	109	113.0	0	0	12.88
5-10cm	5.8	23.9	42.9	8.5	37.9	118.9	116	102.4	0	0	12.99
5-10cm	7.9	24.2	41.5	7.8	39.6	121.0	113	107.1	0	0	12.92
10-15cm	5.9	25.3	33.0	6.1	32.8	103.0	103	100.0	0	0	10.36
10-15cm	5.3	25.5	32.0		38.1	100.8	102	98.6	0	0	10.24
10-15cm	5.2	25.6	33.7	5.2	34.7	104.3	100	103.9	0	0	10.46
10-15cm	5.1	25.0	34.1	4.6	34.0	102.7	104	98.9	0	0	10.28
10-15cm	5.1	24.6	32.2	5.5	32.7	100.0	106	94.5	0	0	10.39
10-15cm	4.8	25.4	33.2	4.9	32.0	100.1	106	94.3	0	0	10.5
15-25cm	4.4	15.1	34.9	6.3	25.2	85.8	78	109.4	0	0	8.06
15-25cm	4.1	14.7	22.4	4.5	28.8	74.5	83	89.7	0	0	8.1
15-25cm	4.0	15.6	32.8	5.2	33.0	90.5	82	110.9	0	0	8.23
15-25cm	4.0	15.4	27.2	4.6	30.3	81.5	75	108.7	0	0	8.03
15-25cm	3.9	15.2	26.8	4.6		50.5	74	68.0	0	0	7.95
15-25cm	3.8	14.8	25.7	4.4	32.2	80.7	78	103.4	0	0	8.08
25-35cm	4.4	7.6	5.7	2.6	22.9	43.2	47	91.7	0	0	6.32
25-35cm	4.4	7.8	6.6	2.6	25.0	46.3	47	98.1	0	0	6.24
25-35cm	4.3	7.6	6.7	2.5	25.4	46.5	43	107.6	0	0	6.14
25-35cm	4.5	7.9	0.0	3.8	23.7	39.9	47	85.0	0	0	6.17
25-35cm	4.4	7.8	6.4	2.8	24.5	45.9	48	95.1	0	0	6.18
25-35cm	4.5	7.9	6.2	2.7	25.1	46.4	53	88.3	0	0	5.99
35-50cm	3.8	3.5	3.1	1.4	13.4	25.2	23	108.2	0	0	5.22
35-50cm	3.8	3.9	5.9	2.2	13.5	29.2	23	125.1	0	0	5.19
35-50cm	3.9	3.6	3.5	1.7	13.9	26.5	22	117.9	0	0	4.64
35-50cm	4.0	3.5	2.8	1.5	13.3	25.0	23	109.2	0	0	4.67
35-50cm	3.9	3.7	3.0	1.4	12.8	24.7	24	103.3	0	0	4.46
35-50cm	3.8	3.6	3.0	1.5	13.5	25.4	23	109.4	0	0	4.64

	HA g g	FA g g	pH	OC %	CEC me/100g	PYR7Fe mg/kg Fe
0-5cm	0.0264	0.0778	6.5	12.8	40.8	2300
0-5cm	0.0282	0.0717	6.5	12.1	41.6	2280
0-5cm	0.0254	0.0737	6.5	11.8	40	2280
0-5cm	0.0250	0.0738	6.6	13.8	40.5	2280
0-5cm	0.0272	0.0822	6.5	12.4	40.65	2340
0-5cm	0.0278	0.0764	6.4	13.3	38.9	2290
5-10cm	0.0220	0.0618	7.1	7.7	28.41	2290
5-10cm	0.0272	0.0674	7.2	7.6	28.62	2200
5-10cm	0.0230	0.0590	7.2	7.7	28.68	2200
5-10cm	0.0198	0.0617	7.2	7.3	28.62	2270
5-10cm	0.0238	0.0623	7.1	7.6	28.47	2310
5-10cm	0.0238	0.0662	7.2	7.5	28.5	2290
10-15cm	0.0174	0.2329	7.3	6.4	28.74	2120
10-15cm	0.0310	0.1542	7.3	6.3	28.77	2180
10-15cm	0.0238	0.0327	7.3	6.3	28.86	2170
10-15cm	0.0248	0.0220	7.3	6.2	28.8	2110
10-15cm	0.0298	0.1565	7.3	6.3	28.68	2150
10-15cm	0.0116	0.1765	7.2	6.3	28.77	2130
15-25cm	0.0194	0.1130	7.1	5.4	29.16	1700
15-25cm	0.0296	0.0279	7.2	5.4	29.04	1670
15-25cm	0.0332	0.0179	7.1	5.5	29.1	1700
15-25cm	0.0276	0.0343	7.2	5.4	29.07	1690
15-25cm	0.0258	0.0521	7.1	5.5	29.16	1700
15-25cm	0.0376	0.1065	7.1	5.3	29.16	1690
25-35cm	0.1012	0.0642	6.4	3.8	27.6	1380
25-35cm	0.1012	0.0692	6.3	3.7	27.66	1340
25-35cm	0.0860	0.6144	6.4	3.7	27.66	1330
25-35cm	0.0996	0.2426	6.4	3.7	27.63	1320
25-35cm	0.1048	0.1831	6.3	3.8	27.63	1350
25-35cm	0.0868	0.3711	6.4	3.7	27.6	1370
35-50cm	0.0472	0.0624	5.7	2.7	27.96	1130
35-50cm	0.0620	0.0537	5.7	2.9	27.81	1120
35-50cm	0.0384	0.0597	5.6	2.7	28.02	1100
35-50cm	0.0644	0.0611	5.7	2.7	28.14	1140
35-50cm	0.0632	0.0635	5.7	2.7	28.17	1140
35-50cm	0.0336	0.0527	5.7	2.7	27.45	1130

RINGINGLOW Site RB Lead

Profile	Exchange mg/kg	Carbonate mg/kg	FMO mg/kg	Organic mg/kg	Residual mg/kg	SUM mg/kg	Digest mg/kg	SUM%D %	HA mg/kg	FA mg/kg	LOI %
0-5cm	56.3	32.5	49.8	25.3	29.8	193.5	230	84.1	4.7	0.35	15.26
0-5cm	58.0	33.0	49.0	25.8	31.8	197.5	240	82.3	5.6	0.45	15.62
0-5cm	64.5	28.0	48.5	24.5	37.3	202.8	230	88.2	4.7	0.55	15.76
0-5cm	65.8	27.8	49.5	25.0	30.8	198.8	240	82.8	3.8	0.45	16.41
0-5cm	65.3	28.7	51.5	26.8	34.5	206.8	240	86.1	5.4	0.3	16.29
0-5cm	44.8	38.0	53.3	26.0	37.3	199.3	230	86.6	4.9	0.45	16.34
5-10cm	52.5	23.8	42.5	21.5	22.8	163.0	190	85.8	6.4	0.55	10.2
5-10cm	49.5	25.5	45.8	22.3	22.3	165.3	190	87.0	3.7	0.65	10.5
5-10cm	55.0	22.3	41.3	22.0	23.3	163.8	180	91.0	2.25	0.65	10.4
5-10cm	46.3	26.3	47.8	23.3	24.5	168.0	190	88.4	5.65	0.6	10.2
5-10cm	54.8	22.3	42.0	21.8	23.8	164.5	190	86.6	4.2	0.55	10
5-10cm	47.0	26.3	44.3	22.5	23.8	163.8	190	86.2	6.25	0.6	9.86
10-15cm	31.0	11.8	22.3	12.5	13.5	91.0	95	95.8	1.85	1.1	5.92
10-15cm	29.3	12.0	18.3	11.5	8.3	79.3	90	88.1	1.8	0.9	5.69
10-15cm	28.7	12.0	17.0	12.3	12.8	82.8	95	87.1	2	0.95	5.69
10-15cm	29.3	11.5	11.0	11.5	8.8	72.0	90	80.0	1.85	0.95	5.76
10-15cm	27.3	11.5	9.3	10.8	12.8	71.5	95	75.3	1.95	1.05	5.8
10-15cm	28.2	11.5	6.5	10.5	8.8	65.5	95	68.9	1.9	1	6.28
15-25cm	17.0	4.5	12.5	6.8	13.3	54.0	50	109.1	0.7	1.45	3.61
15-25cm	19.5	4.0	11.5	6.3	12.5	53.8	50	108.6	1.05	1.35	3.75
15-25cm	16.0	2.3	11.8	6.8	12.3	49.0	55	89.1	1.2	1.45	3.68
15-25cm	17.8	3.3	11.8	6.0	12.3	51.0	55	92.7	0.75	1.45	3.64
15-25cm	17.0	4.0	14.2	7.2	8.8	51.3	50	103.5	0.65	1.45	3.49
15-25cm	16.3	3.8	12.0	5.8	7.5	45.3	50	90.5	0.75	1.5	3.38
25-35cm	28.0	15.0	20.0	10.0	12.5	85.5	93	91.9	0.4	0.75	3.59
25-35cm	25.8	15.0	15.0	7.5	20.0	83.3	104	80.0	0.75	0.7	3.8
25-35cm	27.5	15.0	17.5	10.0	12.5	82.5	100	82.5	0.9	0.6	3.77
25-35cm	24.8	12.5	12.5	7.5	20.0	77.3	100	77.3	0.7	0.8	3.83
25-35cm	27.5	15.0	17.5	7.5	17.5	85.0	97	87.6	0.8	0.7	3.87
25-35cm	28.5	17.5	20.0	10.0		76.0	108	70.4	0.8	0.7	3.7
35-50cm	20.0	12.5	15.0	7.5	15.0	70.0	79	88.6	0.8	0.85	2.74
35-50cm	22.5	12.5	20.0	10.0	25.0	90.0	76	118.4	0.45	0.7	6.33
35-50cm	22.5	12.5	17.5	7.5	22.5	82.5	79	104.4	0.5	0.85	2.77
35-50cm	25.0	15.0	20.0	10.0	17.5	87.5	73	119.9	0.75	0.75	2.65
35-50cm	25.0	15.0	20.0	7.5	20.0	87.5	76	115.1	0.85	0.7	2.7
35-50cm	22.5	12.5	15.0	10.0		60.0	84	71.4	0.85	0.8	5.04

	HA g g	FA g g	pH	OC %	CEC me/100g	PYR7Fe mg/kg Fe	PYR7 mg/kg	NaOH mg/kg	PEFA mg/kg
0-5cm	0.0958	0.0253	4	8.5	12.5	6000	222	75.5	62
0-5cm	0.0475	0.0199	4	8.3	14.5	6130	229	79	61.5
0-5cm	0.0521	0.0451	3.9	8.7	13.75	6120	226	76	63
0-5cm	0.0784	0.0409	3.9	8.6	15.25	5980	226	81.5	51.5
0-5cm	0.0864	0.0372	4	8.1	15.1	6030	222	78	67
0-5cm	0.0896	0.0249	4	8.1	15.55	6100	228	78.5	64
5-10cm	0.0844	0.0133	3.9	5.8	12.35	6070	195	58	47
5-10cm	0.0796	0.0212	4	5.7	15.8	6150	202	61.5	48.5
5-10cm	0.0782	0.0202	3.9	5.8	17.2	6130	196	63	38.5
5-10cm	0.0884	0.0172	4	5.9	15.8	5940	192	60.5	50
5-10cm	0.0842	0.0179	4	5.9	16.6	6070	198	59	42.5
5-10cm	0.0862	0.0216	4	5.7	15.25	5820	190	60.5	49.5
10-15cm	0.0052	0.0246	4	3.8	11.05	3640	117	27	14
10-15cm	0.0064	0.0191	4	4	10.65	3650	118	26	17.5
10-15cm	0.0073	0.0166	4	3.9	9.75	3710	118	25	25
10-15cm	0.0068	0.0250	4	4.1	9.3	3630	121	27	17
10-15cm	0.0054	0.0235	3.9	4	8.4	3580	116	30.5	16
10-15cm	0.0044	0.0173	4	3.8	10.75	3550	116	27.5	22.5
15-25cm	0.0020	0.1042	4	1.8	12.25	2470	86	12	8
15-25cm	0.0028	0.0195	4.1	1.8	14.6	2470	87	12.5	12
15-25cm	0.0054	0.0224	4.1	1.9	12.4	2460	87	13	13
15-25cm	0.0032	0.0045	4.1	1.7	12.2	2540	85	10.5	4
15-25cm	0.0026	0.0431	4.1	1.9	11.65	2510	85	12	11.5
15-25cm	0.0040	0.0494	4	1.8	13.05	2520	85	13	7.5
25-35cm	0.0024	0.1267	4.1	2.3	12.9	2350	89	12	11
25-35cm	0.0024	0.0207	4	2.3	13.15	2340	86	12	11.5
25-35cm	0.0047	0.0202	4.1	2.3	11.75	2430	90	12	13.5
25-35cm	0.0014	0.0231	4.1	2.2	11.95	2360	89	12	14.5
25-35cm	0.0052	0.0778	4.1	2.3	9.5	2330	88	13.5	7.5
25-35cm	0.0030	0.1376	4.1	2.4	13.9	2400	91	12.5	9.5
35-50cm	0.0033	0.1236	4.2	2.7	15	1870	76	9	9
35-50cm	0.0024	0.0203	4.1	2.6	14.2	1840	73	9.5	9.5
35-50cm	0.0039	0.0170	4.2	2.6	11.9	1840	73	9	0.5
35-50cm	0.0052	0.0255	4.1	2.6	13.35	1880	74	9	9.5
35-50cm	0.0036	0.1005	4.2	2.6	11.45	1850	71	9.5	6.5
35-50cm	0.0034	0.0694	4.2	2.5	12.15	1820	72	9	1

RINGINGLOW Site RB Zinc

Profile	Exchange mg/kg	Carbonate mg/kg	FMO mg/kg	Organic mg/kg	Residual mg/kg	SUM mg/kg	Digest mg/kg	SUM%D %	HA mg/kg	FA mg/kg	LOI %
0-5cm	8.0	4.0	8.0	7.8	32.5	60.3	74	81.4	0.85	0.2	15.26
0-5cm	7.2	4.0	8.0	8.5	34.0	61.8	76	81.3	0.7	0.2	15.62
0-5cm	8.0	3.3	7.8	8.0	35.3	62.3	76	81.9	0.65	0.15	15.76
0-5cm	8.3	3.0	8.0	7.8	32.0	59.0	75	78.7	0.5	0.2	16.41
0-5cm	8.0	3.3	8.0	9.0	34.5	62.8	75	83.7	0.8	0.2	16.29
0-5cm	6.3	4.5	8.3	8.0	36.5	63.5	75	84.7	0.7	0.2	16.34
5-10cm	6.0	3.0	8.3	6.8	30.5	54.5	62	87.9	1.15	0.2	10.2
5-10cm	5.3	3.0	8.3	6.8	30.0	53.3	62	85.9	0.85	0.25	10.5
5-10cm	5.8	2.8	7.2	7.0	31.0	53.8	60	89.6	0.85	0.2	10.4
5-10cm	5.0	3.3	7.5	7.0	29.0	51.8	62	83.5	1.15	0.25	10.2
5-10cm	5.8	2.8	7.2	7.0	29.5	52.3	62	84.3	1.05	0.25	10
5-10cm	5.0	3.3	7.5	6.5	29.5	51.8	61	84.8	1	0.2	9.86
10-15cm	7.2	6.5	7.5	8.8	25.0	55.0	57	95.7	0.55	0.5	5.92
10-15cm	6.3	5.8	7.2	8.5	26.0	53.8	56	95.1	0.4	0.5	5.69
10-15cm	7.8	5.0	7.2	8.8	29.0	57.7	57	100.4	0.4	0.4	5.69
10-15cm	6.5	4.3	7.2	8.8	24.8	51.5	56	91.2	0.5	0.5	5.76
10-15cm	6.5	5.0	7.2	13.5	27.5	59.8	56	106.7	0.45	0.55	5.8
10-15cm	7.2	4.3	7.5	8.3	26.5	53.8	56	96.0	0.55	0.45	6.28
15-25cm	6.3	5.0	7.5	8.3	29.3	56.3	65	86.5	0.35	0.8	3.61
15-25cm	6.3	6.0	6.5	8.3	31.0	58.0	66	87.9	0.35	0.7	3.75
15-25cm	5.0	4.8	7.0	8.3	30.0	55.0	61	90.2	0.45	0.65	3.66
15-25cm	5.8	5.0	7.0	9.5	31.3	58.5	65	90.0	0.35	0.65	3.64
15-25cm	6.0	5.3	7.0	7.5	30.8	56.5	64	88.3	0.4	0.8	3.49
15-25cm	5.8	5.3	7.2	7.2	25.0	50.5	63	80.2	0.4	0.7	3.38
25-35cm	3.8	2.0	5.0	5.5	21.0	37.3	38	97.0	0.35	0.35	3.59
25-35cm	3.8	2.0	5.3	6.3	21.8	39.0	38	103.2	0.4	0.3	3.8
25-35cm	3.8	2.3	5.0	5.3	22.0	38.3	37	102.8	0.5	0.35	3.77
25-35cm	3.8	2.0	6.3	5.0	21.8	38.8	37	104.2	0.35	0.35	3.83
25-35cm	4.0	2.0	6.8	5.5	22.8	41.0	38	106.8	0.3	0.3	3.87
25-35cm	3.8	2.3	7.5	5.3		18.8	38	48.8	0.35	0.35	3.7
35-50cm	5.5	3.0	7.0	5.3	20.8	41.5	42	98.8	0.5	0.4	2.74
35-50cm	6.8	3.5	8.3	5.5	20.8	44.8	42	106.5	0.4	0.35	6.33
35-50cm	5.0	3.0	6.3	4.5	20.5	39.3	42	93.5	0.45	0.5	2.77
35-50cm	5.8	3.5	6.5	5.0	22.3	43.0	42	103.6	0.45	0.5	2.65
35-50cm	5.0	2.8	6.5	4.8	19.5	38.5	42	92.8	0.45	0.45	2.7
35-50cm	5.5	3.3	7.0	4.8		20.5	42	48.8	0.45	0.4	5.04

	HA g g	FA g g	pH	OC %	CEC me/100g	PYR7Fe mg/kg Fe	PYR7 mg/kg
0-5cm	0.0958	0.0253	4	8.5	12.5	6000	73
0-5cm	0.0475	0.0199	4	8.3	14.5	6130	73
0-5cm	0.0521	0.0451	3.9	8.7	13.75	6120	73
0-5cm	0.0784	0.0409	3.9	8.6	15.25	5980	73
0-5cm	0.0864	0.0372	4	8.1	15.1	6030	74
0-5cm	0.0896	0.0249	4	8.1	15.55	6100	73
5-10cm	0.0844	0.0133	3.9	5.8	12.35	6070	69
5-10cm	0.0796	0.0212	4	5.7	15.8	6150	70
5-10cm	0.0782	0.0202	3.9	5.8	17.2	6130	69
5-10cm	0.0884	0.0172	4	5.9	15.8	5940	69
5-10cm	0.0842	0.0179	4	5.9	16.6	6070	69
5-10cm	0.0862	0.0216	4	5.7	15.25	5820	68
10-15cm	0.0052	0.0246	4	3.8	11.05	3640	66
10-15cm	0.0064	0.0191	4	4	10.65	3650	66
10-15cm	0.0073	0.0166	4	3.9	9.75	3710	64
10-15cm	0.0068	0.0250	4	4.1	9.3	3630	66
10-15cm	0.0054	0.0235	3.9	4	8.4	3580	65
10-15cm	0.0044	0.0173	4	3.8	10.75	3550	64
15-25cm	0.0020	0.1042	4	1.8	12.25	2470	65
15-25cm	0.0028	0.0195	4.1	1.8	14.6	2470	65
15-25cm	0.0054	0.0224	4.1	1.9	12.4	2460	64
15-25cm	0.0032	0.0045	4.1	1.7	12.2	2540	65
15-25cm	0.0026	0.0431	4.1	1.9	11.65	2510	65
15-25cm	0.0040	0.0494	4	1.8	13.05	2520	64
25-35cm	0.0024	0.1267	4.1	2.3	12.9	2350	64
25-35cm	0.0024	0.0207	4	2.3	13.15	2340	65
25-35cm	0.0047	0.0202	4.1	2.3	11.75	2430	66
25-35cm	0.0014	0.0231	4.1	2.2	11.95	2360	65
25-35cm	0.0052	0.0778	4.1	2.3	9.5	2330	65
25-35cm	0.0030	0.1376	4.1	2.4	13.9	2400	65
35-50cm	0.0033	0.1236	4.2	2.7	15	1870	66
35-50cm	0.0024	0.0203	4.1	2.6	14.2	1840	64
35-50cm	0.0039	0.0170	4.2	2.6	11.9	1840	63
35-50cm	0.0052	0.0255	4.1	2.6	13.35	1880	66
35-50cm	0.0036	0.1005	4.2	2.6	11.45	1850	64
35-50cm	0.0034	0.0694	4.2	2.5	12.15	1820	65

RINGINGLOW Site RB Copper

Profile	Exchange mg/kg	Carbonate mg/kg	FMO mg/kg	Organic mg/kg	Residual mg/kg	SUM mg/kg	Digest mg/kg	SUM%D %	HA mg/kg	FA mg/kg	LOI %
0-5cm	4.5	3.5	3.5	15.3	13.5	40.3	41	98.2	8.1	0.3	15.26
0-5cm	4.5	3.3	3.5	15.8	14.2	41.3	41	100.6	7.2	0.55	15.62
0-5cm	4.8	3.3	3.5	15.5	15.3	42.3	40	105.6	7.1	0.4	15.76
0-5cm	4.8	3.3	3.8	15.5	13.5	40.8	42	97.0	7.3	0.35	16.41
0-5cm	5.0	3.3	3.3	16.3	14.0	41.8	43	97.1	6.7	0.25	16.29
0-5cm	4.8	3.3	2.5	15.8	15.3	41.5	41	101.2	7.8	0.45	16.34
5-10cm	3.3	3.5	3.8	12.8	12.5	35.8	36	99.3	7.4	0.85	10.2
5-10cm	3.0	3.3	3.8	12.8	12.5	35.3	36	97.9	5.4	0.6	10.5
5-10cm	3.3	3.3	3.5	13.5	13.8	37.3	35	106.4	3.95	0.65	10.4
5-10cm	3.3	3.3	3.8	13.0	11.8	35.0	35	100.0	5.85	0.5	10.2
5-10cm	3.5	3.3	3.8	13.8	12.5	36.8	35	105.0	2.9	0.45	10
5-10cm	3.3	3.3	3.5	13.0	12.8	35.8	35	102.1	5.7	0.8	9.86
10-15cm	3.3	2.8	3.0	7.5	6.0	22.5	22	104.7	3.75	0.65	5.92
10-15cm	3.0	2.8	2.8	7.0	6.0	21.5	21	104.9	3.7	0.85	5.69
10-15cm	3.0	2.8	2.8	7.2	6.3	22.0	24	91.7	4.05	0.65	5.69
10-15cm	3.0	2.8	3.0	7.2	5.8	21.8	21	103.6	3.8	0.7	5.76
10-15cm	3.0	2.8	3.0	7.5	6.0	22.3	22	103.5	3.65	0.6	5.8
10-15cm	2.8	3.0	3.0	7.2	6.3	22.3	22	103.5	3.7	0.65	6.28
15-25cm	3.0	3.0	2.8	5.3	7.2	21.3	24	88.5	1.75	0.75	3.61
15-25cm	3.0	2.8	3.0	5.5	8.3	22.5	24	93.8	1.75	1	3.75
15-25cm	3.0	2.8	3.0	5.3	8.0	22.0	23	95.7	2.55	0.9	3.66
15-25cm	2.8	3.0	2.8	5.0	8.5	22.0	23	95.7	1.9	0.9	3.64
15-25cm	3.0	2.8	2.8	5.5	7.8	21.8	22	98.9	2.35	0.85	3.49
15-25cm	2.8	3.0	3.0	4.8	8.5	22.0	24	91.7	2.2	0.95	3.38
25-35cm	2.8	3.0	3.0	5.5	6.3	20.5	25	82.0	1.35	0.5	3.59
25-35cm	3.0	3.3	3.0	6.0	6.5	21.8	24	90.6	1.45	0.65	3.8
25-35cm	3.3	2.8	3.0	6.0	6.8	21.8	23	94.6	2	0.8	3.77
25-35cm	2.8	2.8	3.3	6.5	6.3	21.5	24	89.6	1.9	0.75	3.83
25-35cm	4.5	3.0	3.0	6.3	6.5	23.3	26	89.4	1.85	1.05	3.87
25-35cm	3.0	3.0	3.3	6.8		16.0	25	64.0	2.15	0.75	3.7
35-50cm	2.8	2.5	3.0	5.3	5.8	19.3	20	96.3	1.2	0.75	2.74
35-50cm	3.0	2.8	3.3	4.8	5.5	19.3	22	87.5	1.55	0.65	6.33
35-50cm	3.5	2.8	2.8	4.8	5.5	19.3	20	96.3	1.35	0.75	2.77
35-50cm	3.0	3.8	3.0	5.3	6.5	21.5	20	107.5	1.6	0.7	2.65
35-50cm	3.8	3.0	2.8	5.3	5.5	20.3	19	106.6	1.35	0.75	2.7
35-50cm	3.0	2.5	2.5	4.8		12.8	21	60.7	1.35	0.65	5.04

	HA g g	FA g g	pH	OC %	CEC me/100g	PYR7Fe mg/kg Fe	PYR7 mg/kg	NaOH mg/kg	PEFA mg/kg
0-5cm	0.0958	0.0253	4	8.5	12.5	6000	24	23	13.5
0-5cm	0.0475	0.0199	4	8.3	14.5	6130	26	23.5	17.5
0-5cm	0.0521	0.0451	3.9	8.7	13.75	6120	25	23	16.5
0-5cm	0.0784	0.0409	3.9	8.6	15.25	5980	24	24	16
0-5cm	0.0864	0.0372	4	8.1	15.1	6030	25	23.5	13.5
0-5cm	0.0896	0.0249	4	8.1	15.55	6100	24	23.5	25.5
5-10cm	0.0844	0.0133	3.9	5.8	12.35	6070	22	22	19.5
5-10cm	0.0796	0.0212	4	5.7	15.8	6150	22	23	12
5-10cm	0.0782	0.0202	3.9	5.8	17.2	6130	21	22	19.5
5-10cm	0.0884	0.0172	4	5.9	15.8	5940	22	22.5	27.5
5-10cm	0.0842	0.0179	4	5.9	16.6	6070	21	21	18.5
5-10cm	0.0862	0.0216	4	5.7	15.25	5820	21	21	16
10-15cm	0.0052	0.0246	4	3.8	11.05	3640	17	12	4
10-15cm	0.0064	0.0191	4	4	10.65	3650	17	12	12
10-15cm	0.0073	0.0166	4	3.9	9.75	3710	15	12	8.5
10-15cm	0.0068	0.0250	4	4.1	9.3	3630	17	12	11.5
10-15cm	0.0054	0.0235	3.9	4	8.4	3580	17	13	8.5
10-15cm	0.0044	0.0173	4	3.8	10.75	3550	16	12	13.5
15-25cm	0.0020	0.1042	4	1.8	12.25	2470	13	8	7.5
15-25cm	0.0028	0.0195	4.1	1.8	14.6	2470	13	7.5	7
15-25cm	0.0054	0.0224	4.1	1.9	12.4	2460	14	7.5	4
15-25cm	0.0032	0.0045	4.1	1.7	12.2	2540	14	7.5	8
15-25cm	0.0026	0.0431	4.1	1.9	11.65	2510	14	7.5	6
15-25cm	0.0040	0.0494	4	1.8	13.05	2520	14	7	3.5
25-35cm	0.0024	0.1267	4.1	2.3	12.9	2350	14	7	4
25-35cm	0.0024	0.0207	4	2.3	13.15	2340	14	7	7
25-35cm	0.0047	0.0202	4.1	2.3	11.75	2430	14	8	2
25-35cm	0.0014	0.0231	4.1	2.2	11.95	2360	15	7.5	3
25-35cm	0.0052	0.0778	4.1	2.3	9.5	2330	14	7	7
25-35cm	0.0030	0.1376	4.1	2.4	13.9	2400	15	7.5	2.5
35-50cm	0.0033	0.1236	4.2	2.7	15	1870	12	6	1.5
35-50cm	0.0024	0.0203	4.1	2.6	14.2	1840	12	7.5	2.5
35-50cm	0.0039	0.0170	4.2	2.6	11.9	1840	12	5	4.5
35-50cm	0.0052	0.0255	4.1	2.6	13.35	1880	13	6.5	1.5
35-50cm	0.0036	0.1005	4.2	2.6	11.45	1850	12	4.5	6.5
35-50cm	0.0034	0.0694	4.2	2.5	12.15	1820	12	7.5	0.5

RINGINGLOW Site RB Nickel

Profile	Exchange mg/kg	Carbonate mg/kg	FMO mg/kg	Organic mg/kg	Residual mg/kg	SUM mg/kg	Digest mg/kg	SUM%D %	HA mg/kg	FA mg/kg	LOI %
0-5cm	6.8	5.3	0.0	0.0	111.5	123.5	67	184.3	1.35	0	15.26
0-5cm	6.0	8.0	0.0	0.0	41.0	55.0	82	67.1	1.05	0	15.62
0-5cm	5.8	4.3	0.0	0.0	77.8	87.8	75	117.0	0.95	0	15.76
0-5cm	7.0	5.3	0.0	0.0	34.3	46.5	75	62.0	1.4	0	16.41
0-5cm	5.8	4.8	0.0	0.0	87.8	98.3	75	131.0	1.3	0	16.29
0-5cm	8.0	5.3	0.0	0.0	64.5	77.8	80	97.2	1.25	0	16.34
5-10cm	6.5	5.3	0.0	0.0	93.8	105.5	98	107.7	1.45	0	10.2
5-10cm	5.5	6.3	0.0	0.0	49.3	61.0	67	91.0	1.5	0	10.5
5-10cm	6.3	5.3	0.0	0.0	87.8	99.3	80	124.1	1.4	0	10.4
5-10cm	5.8	5.0	0.0	0.0	93.0	103.8	89	116.6	1.4	0	10.2
5-10cm	5.8	4.8	0.0	0.0	71.5	82.0	87	94.3	1.5	0	10
5-10cm	6.5	4.8	0.0	0.0	71.0	82.3	73	112.7	1.6	0	9.86
10-15cm	5.5	4.5	0.0	0.0	19.5	29.5	26	115.7	1.05	0.7	5.92
10-15cm	5.8	5.0	0.0	0.0	19.3	30.0	27	113.2	0.75	0.65	5.69
10-15cm	6.5	4.8	0.0	0.0	21.8	33.0	29	113.8	0.7	0.75	5.69
10-15cm	6.3	4.8	0.0	0.0	19.8	30.8	24	130.9	0.9	0.8	5.76
10-15cm	6.0	4.8	0.0	0.0	18.5	29.3	40	73.1	0.65	0.7	5.8
10-15cm	6.3	5.0	0.0	0.0	18.8	30.0	31	96.8	0.9	0.75	6.28
15-25cm	6.8	4.5	0.0	0.0	24.8	36.0	27	133.3	1	1.3	3.61
15-25cm	5.5	4.5	0.0	0.0	20.3	30.3	30	102.5	0.8	1.45	3.75
15-25cm	8.3	4.5	0.0	0.0	17.5	30.3	21	144.0	0.95	1.05	3.66
15-25cm	4.8	4.5	0.0	0.0	18.8	28.0	26	109.8	0.95	1.1	3.64
15-25cm	5.0	4.3	0.0	0.0	17.5	26.8	24	111.5	1.1	1.25	3.49
15-25cm	5.5	4.0	0.0	0.0	21.5	31.0	23	137.8	1	1.3	3.38
25-35cm	7.0	0.0	0.0	0.0	12.3	19.3	21	93.9	0.4	0	3.59
25-35cm	7.2	0.0	0.0	0.0	14.8	22.0	17	129.4	0.95	0	3.8
25-35cm	7.0	0.0	0.0	0.0	13.0	20.0	18	114.3	1.4	0	3.77
25-35cm	6.8	0.0	0.0	0.0	14.8	21.5	18	119.4	1.65	0	3.83
25-35cm	6.8	0.0	0.0	0.0	11.8	18.5	18	105.7	0.7	0	3.87
25-35cm	7.5	0.0	0.0	0.0		7.5	17	44.1	1.05	0	3.7
35-50cm	12.5	0.0	0.0	0.0	8.5	21.0	14	150.0	0.9	0.8	2.74
35-50cm	6.5	0.0	0.0	0.0	10.0	16.5	14	122.2	0.9	0.35	6.33
35-50cm	6.3	0.0	0.0	0.0	8.8	15.0	16	93.8	0.95	0.5	2.77
35-50cm	6.5	0.0	0.0	0.0	10.0	16.5	20	84.6	0.95	0.55	2.65
35-50cm	6.3	0.0	0.0	0.0	12.0	18.3	16	114.1	0.9	0.6	2.7
35-50cm	7.0	0.0	0.0	0.0		7.0	22	32.6	0.9	0.7	5.04

	HA g g	FA g g	pH	OC %	CEC me/100g	PYR7Fe mg/kg Fe
0-5cm	0.0958	0.0253	4	8.5	12.5	6000
0-5cm	0.0475	0.0199	4	8.3	14.5	6130
0-5cm	0.0521	0.0451	3.9	8.7	13.75	6120
0-5cm	0.0784	0.0409	3.9	8.6	15.25	5980
0-5cm	0.0864	0.0372	4	8.1	15.1	6030
0-5cm	0.0896	0.0249	4	8.1	15.55	6100
5-10cm	0.0844	0.0133	3.9	5.8	12.35	6070
5-10cm	0.0796	0.0212	4	5.7	15.8	6150
5-10cm	0.0782	0.0202	3.9	5.8	17.2	6130
5-10cm	0.0884	0.0172	4	5.9	15.8	5940
5-10cm	0.0842	0.0179	4	5.9	16.6	6070
5-10cm	0.0862	0.0216	4	5.7	15.25	5820
10-15cm	0.0052	0.0246	4	3.8	11.05	3640
10-15cm	0.0064	0.0191	4	4	10.65	3650
10-15cm	0.0073	0.0166	4	3.9	9.75	3710
10-15cm	0.0068	0.0250	4	4.1	9.3	3630
10-15cm	0.0054	0.0235	3.9	4	8.4	3580
10-15cm	0.0044	0.0173	4	3.8	10.75	3550
15-25cm	0.0020	0.1042	4	1.8	12.25	2470
15-25cm	0.0028	0.0195	4.1	1.8	14.6	2470
15-25cm	0.0054	0.0224	4.1	1.9	12.4	2460
15-25cm	0.0032	0.0045	4.1	1.7	12.2	2540
15-25cm	0.0026	0.0431	4.1	1.9	11.65	2510
15-25cm	0.0040	0.0494	4	1.8	13.05	2520
25-35cm	0.0024	0.1267	4.1	2.3	12.9	2350
25-35cm	0.0024	0.0207	4	2.3	13.15	2340
25-35cm	0.0047	0.0202	4.1	2.3	11.75	2430
25-35cm	0.0014	0.0231	4.1	2.2	11.95	2360
25-35cm	0.0052	0.0778	4.1	2.3	9.5	2330
25-35cm	0.0030	0.1376	4.1	2.4	13.9	2400
35-50cm	0.0033	0.1236	4.2	2.7	15	1870
35-50cm	0.0024	0.0203	4.1	2.6	14.2	1840
35-50cm	0.0039	0.0170	4.2	2.6	11.9	1840
35-50cm	0.0052	0.0255	4.1	2.6	13.35	1880
35-50cm	0.0036	0.1005	4.2	2.6	11.45	1850
35-50cm	0.0034	0.0694	4.2	2.5	12.15	1820

RINGINGLOW Site RB Iron

Profile	Exchange mg/kg	Carbonate mg/kg	FMO mg/kg	Organic mg/kg	Residual mg/kg	SUM mg/kg	Digest mg/kg	SUM%D %	HA mg/kg	FA mg/kg	LOI %
0-5cm	129.5	259.5	4127.5	1650.0	9437.5	15604.0	18210	85.7	225.5	17.5	15.26
0-5cm	136.0	271.5	4012.5	1865.0	9860.0	16145.0	19040	84.8	301	12	15.62
0-5cm	154.3	232.5	4020.0	1697.5	10452.5	16556.8	18320	90.4	220	10.5	15.76
0-5cm	159.0	226.3	4107.5	1775.0	9137.5	15405.3	18290	84.2	293.75	13.35	16.41
0-5cm	151.3	239.5	4117.5	1977.5	9797.5	16283.3	18750	86.8	244.85	11.85	16.29
0-5cm	102.0	259.0	4035.0	1727.5	10300.0	16423.5	18130	90.6	299.8	9.55	16.34
5-10cm	118.8	329.0	4852.5	1450.0	10442.5	17192.8	18640	92.2	525.5	3	10.2
5-10cm	105.5	323.5	4772.5	1455.0	10392.5	17049.0	17730	96.2	527.5	9.5	10.5
5-10cm	124.3	317.3	4647.5	1465.0	10590.0	17144.0	17600	97.4	482.5	1.5	10.4
5-10cm	102.8	332.0	4852.5	1455.0	9502.5	16244.8	17750	91.5	435.1	1.65	10.2
5-10cm	123.3	311.8	4877.5	1495.0	10335.0	17142.5	17970	95.4	525	8.95	10
5-10cm	100.5	325.8	4700.0	1425.0	10255.0	16806.3	18100	92.9	503.3	0.35	9.86
10-15cm	115.0	235.0	3535.0	847.5	7647.5	12380.0	14780	83.8	143.5	4.5	5.92
10-15cm	120.0	222.5	3542.5	867.5	7902.5	12655.0	14515	87.2	72.5	2.5	5.69
10-15cm	110.0	227.5	3460.0	852.5	8225.0	12875.0	14405	89.4	131.5	2.5	5.69
10-15cm	117.5	235.0	3650.0	867.5	7632.5	12502.5	14215	88.0	163.3	5.75	5.76
10-15cm	117.5	227.5	3672.5	880.0	7830.0	12727.5	14375	88.5	99.7	3.85	5.8
10-15cm	120.0	235.0	3625.0	847.5	7830.0	12657.5	14315	88.4	102.55	3.35	6.28
15-25cm	92.5	175.0	2707.5	490.0	7585.0	11050.0	12090	91.4	40	13.5	3.61
15-25cm	70.0	190.0	2742.5	520.0	8440.0	11962.5	12400	96.5	50	9	3.75
15-25cm	82.5	170.0	2745.0	540.0	8082.5	11620.0	12255	94.8	70.5	15.5	3.66
15-25cm	82.5	177.5	2707.5	512.5	8270.0	11750.0	12055	97.5	35.9	14	3.64
15-25cm	75.0	190.0	2780.0	535.0	8245.0	11825.0	11930	99.1	56.4	11.5	3.49
15-25cm	72.5	182.5	2827.5	525.0	8137.5	11745.0	11825	99.3	65.1	17.25	3.38
25-35cm	70.0	202.5	2710.0	430.0	6440.0	9852.5	11310	87.1	59	3.5	3.59
25-35cm	67.5	187.5	2735.0	440.0	6797.5	10227.5	11085	92.3	71	3.5	3.8
25-35cm	70.0	197.5	2920.0	450.0	6992.5	10630.0	11000	96.6	69	4	3.77
25-35cm	72.5	197.5	2852.5	460.0	6880.0	10462.5	10965	95.4	74	3.7	3.83
25-35cm	72.5	197.5	2792.5	467.5	7462.5	10992.5	11315	97.1	64.55	4.55	3.87
25-35cm	70.0	205.0	2892.5	507.5		3675.0	11525	31.9	78.35	3.85	3.7
35-50cm	55.0	162.5	2827.5	372.5	6547.5	9965.0	10620	93.8	36	5	2.74
35-50cm	55.0	175.0	2622.5	352.5	6595.0	9800.0	10765	91.0	30.5	2.5	6.33
35-50cm	110.0	197.5	2625.0	292.5	6650.0	9875.0	10645	92.8	48.5	4	2.77
35-50cm		167.5	2690.0	350.0	6957.5	10165.0	10665	95.3	43.05	4.65	2.65
35-50cm		190.0	2680.0	332.5	6515.0	9717.5	10605	91.6	62.15	4.65	2.7
35-50cm		162.5	2802.5	350.0		3315.0	11105	29.9	30.2	3.75	5.04

	HA g g	FA g g	pH	OC %	CEC me/100g	PYR7Fe mg/kg Fe	PYR7 mg/kg	NaOH mg/kg	PEFA mg/kg
0-5cm	0.0958	0.0253	4	8.5	12.5	6000		2550	1517.5
0-5cm	0.0475	0.0199	4	8.3	14.5	6130		2705	1371
0-5cm	0.0521	0.0451	3.9	8.7	13.75	6120		2625	1423.5
0-5cm	0.0784	0.0409	3.9	8.6	15.25	5980		2735	1367
0-5cm	0.0864	0.0372	4	8.1	15.1	6030		2700	1046
0-5cm	0.0896	0.0249	4	8.1	15.55	6100		2630	1305
5-10cm	0.0844	0.0133	3.9	5.8	12.35	6070		2275	657
5-10cm	0.0796	0.0212	4	5.7	15.8	6150		2410	274
5-10cm	0.0782	0.0202	3.9	5.8	17.2	6130		2535	368
5-10cm	0.0884	0.0172	4	5.9	15.8	5940		2365	68.5
5-10cm	0.0842	0.0179	4	5.9	16.6	6070		2240	71.5
5-10cm	0.0862	0.0216	4	5.7	15.25	5820		2442	350.5
10-15cm	0.0052	0.0246	4	3.8	11.05	3640		1260	320.5
10-15cm	0.0064	0.0191	4	4	10.65	3650		1185	5
10-15cm	0.0073	0.0166	4	3.9	9.75	3710		1210	362
10-15cm	0.0068	0.0250	4	4.1	9.3	3630		1220	133
10-15cm	0.0054	0.0235	3.9	4	8.4	3580		1465	39
10-15cm	0.0044	0.0173	4	3.8	10.75	3550		1428.5	47
15-25cm	0.0020	0.1042	4	1.8	12.25	2470		650	85.5
15-25cm	0.0028	0.0195	4.1	1.8	14.6	2470		600	91
15-25cm	0.0054	0.0224	4.1	1.9	12.4	2460		660	24
15-25cm	0.0032	0.0045	4.1	1.7	12.2	2540		615	152.5
15-25cm	0.0026	0.0431	4.1	1.9	11.65	2510		620	96.5
15-25cm	0.0040	0.0494	4	1.8	13.05	2520		615.5	134
25-35cm	0.0024	0.1267	4.1	2.3	12.9	2350		655	110.5
25-35cm	0.0024	0.0207	4	2.3	13.15	2340		650	106.5
25-35cm	0.0047	0.0202	4.1	2.3	11.75	2430		650	80.5
25-35cm	0.0014	0.0231	4.1	2.2	11.95	2360		655	102.5
25-35cm	0.0052	0.0778	4.1	2.3	9.5	2330		645	90
25-35cm	0.0030	0.1376	4.1	2.4	13.9	2400		644	106
35-50cm	0.0033	0.1236	4.2	2.7	15	1870		550	146.5
35-50cm	0.0024	0.0203	4.1	2.6	14.2	1840		540	120
35-50cm	0.0039	0.0170	4.2	2.6	11.9	1840		600	32.5
35-50cm	0.0052	0.0255	4.1	2.6	13.35	1880		565	32
35-50cm	0.0036	0.1005	4.2	2.6	11.45	1850		590	77.5
35-50cm	0.0034	0.0694	4.2	2.5	12.15	1820		584.5	126.5

RINGINGLOW Site RB Manganese

Profile	Exchange mg/kg	Carbonate mg/kg	FMO mg/kg	Organic mg/kg	Residual mg/kg	SUM mg/kg	Digest mg/kg	SUM%D %	HA mg/kg	FA mg/kg	LOI %
0-5cm	34.8	19.0	21.8	5.0	36.5	117.0	132	88.6	0	0	15.26
0-5cm	35.3	20.0	31.5	5.8	37.8	130.3	144	90.5	0	0	15.62
0-5cm	40.3	13.8	21.5	5.0	41.0	121.5	140	86.8	0	0	15.76
0-5cm	40.8	13.8	21.3	5.0	36.3	117.0	139	84.2	0	0	16.41
0-5cm	40.5	14.2	22.3	5.5	38.0	120.5	140	86.1	0	0	16.29
0-5cm	28.5	26.0	26.0	5.8	42.3	128.5	137	93.8	0	0	16.34
5-10cm	58.3	21.8	30.3	4.8	36.5	151.5	169	89.6	0	0	10.2
5-10cm	52.5	28.5	31.0	5.0	37.0	154.0	167	92.2	0	0	10.5
5-10cm	59.8	21.8	29.3	5.0	37.8	153.5	158	97.2	0	0	10.4
5-10cm	49.8	32.3	32.3	5.3	34.5	154.0	166	92.8	0	0	10.2
5-10cm	59.8	23.0	31.8	5.5	36.3	156.3	168	93.0	0	0	10
5-10cm	49.0	30.5	30.5	5.3	36.3	151.5	163	92.9	0	0	9.86
10-15cm	23.3	6.8	27.3	4.0	27.0	88.3	92	96.4	0	0	5.92
10-15cm	23.0	7.2	21.0	4.0	28.5	83.8	88	95.7	0	0	5.69
10-15cm	22.5	7.2	21.3	4.3	29.3	84.5	88	96.6	0	0	5.69
10-15cm	23.3	7.5	21.3	4.5	28.7	85.3	86	99.7	0	0	5.76
10-15cm	23.0	7.2	23.0	5.0	30.5	88.8	85	104.4	0	0	5.8
10-15cm	23.3	7.5	21.3	4.8	29.3	86.0	110	78.5	0	0	6.28
15-25cm	9.8	3.3	32.8	3.0	28.7	77.5	82	95.1	0	0	3.61
15-25cm	9.8	3.5	31.3	3.8	32.8	81.0	69	118.2	0	0	3.75
15-25cm	10.5	3.0	21.0	3.5	31.0	69.0	68	102.2	0	0	3.66
15-25cm	9.8	3.8	20.0	3.8	34.8	72.0	65	111.6	0	0	3.64
15-25cm	10.3	4.0	22.8	4.5	33.3	74.8	62	120.6	0	0	3.49
15-25cm	10.5	4.3	23.3	4.8	34.5	77.3	60	129.8	0	0	3.38
25-35cm	14.2	4.8	27.3	2.5	21.5	70.3	67	105.6	0	0	3.59
25-35cm	14.0	5.0	22.0	2.3	23.5	66.8	65	103.5	0	0	3.8
25-35cm	15.0	5.0	25.3	2.8	24.0	72.0	85	85.2	0	0	3.77
25-35cm	15.8	6.0	78.3	4.5	23.5	128.0	62	208.1	0	0	3.83
25-35cm	15.8	5.8	22.5	3.0	25.3	72.3	67	108.6	0	0	3.87
25-35cm	15.8	6.8	24.5	3.0		50.0	70	71.4	0	0	3.7
35-50cm	7.8	2.8	28.5	2.3	21.5	62.8	76	83.0	0	0	2.74
35-50cm	8.3	3.3	45.3	2.8	23.8	83.3	75	111.1	0	0	6.33
35-50cm	8.8	3.5	30.0	2.3	21.8	66.3	74	90.0	0	0	2.77
35-50cm	8.8	4.0	29.5	2.5	25.8	70.5	72	97.6	0	0	2.65
35-50cm	9.3	4.5	87.5	4.0	24.5	129.8	75	173.2	0	0	2.7
35-50cm	9.8	4.3	30.5	2.8		47.3	90	52.6	0	0	5.04

	HA g g	FA g g	pH	OC %	CEC me/100g	PYR7Fe mg/kg Fe
0-5cm	0.0958	0.0253	4	8.5	12.5	6000
0-5cm	0.0475	0.0199	4	8.3	14.5	6130
0-5cm	0.0521	0.0451	3.9	8.7	13.75	6120
0-5cm	0.0784	0.0409	3.9	8.6	15.25	5980
0-5cm	0.0864	0.0372	4	8.1	15.1	6030
0-5cm	0.0896	0.0249	4	8.1	15.55	6100
5-10cm	0.0844	0.0133	3.9	5.8	12.35	6070
5-10cm	0.0796	0.0212	4	5.7	15.8	6150
5-10cm	0.0782	0.0202	3.9	5.8	17.2	6130
5-10cm	0.0884	0.0172	4	5.9	15.8	5940
5-10cm	0.0842	0.0179	4	5.9	16.6	6070
5-10cm	0.0862	0.0216	4	5.7	15.25	5820
10-15cm	0.0052	0.0246	4	3.8	11.05	3640
10-15cm	0.0064	0.0191	4	4	10.65	3650
10-15cm	0.0073	0.0166	4	3.9	9.75	3710
10-15cm	0.0068	0.0250	4	4.1	9.3	3630
10-15cm	0.0054	0.0235	3.9	4	8.4	3580
10-15cm	0.0044	0.0173	4	3.8	10.75	3550
15-25cm	0.0020	0.1042	4	1.8	12.25	2470
15-25cm	0.0028	0.0195	4.1	1.8	14.6	2470
15-25cm	0.0054	0.0224	4.1	1.9	12.4	2460
15-25cm	0.0032	0.0045	4.1	1.7	12.2	2540
15-25cm	0.0026	0.0431	4.1	1.9	11.65	2510
15-25cm	0.0040	0.0494	4	1.8	13.05	2520
25-35cm	0.0024	0.1267	4.1	2.3	12.9	2350
25-35cm	0.0024	0.0207	4	2.3	13.15	2340
25-35cm	0.0047	0.0202	4.1	2.3	11.75	2430
25-35cm	0.0014	0.0231	4.1	2.2	11.95	2360
25-35cm	0.0052	0.0778	4.1	2.3	9.5	2330
25-35cm	0.0030	0.1376	4.1	2.4	13.9	2400
35-50cm	0.0033	0.1236	4.2	2.7	15	1870
35-50cm	0.0024	0.0203	4.1	2.6	14.2	1840
35-50cm	0.0039	0.0170	4.2	2.6	11.9	1840
35-50cm	0.0052	0.0255	4.1	2.6	13.35	1880
35-50cm	0.0036	0.1005	4.2	2.6	11.45	1850
35-50cm	0.0034	0.0694	4.2	2.5	12.15	1820

RINGINGLOW Site SRG Lead

Profile	Exchange mg/kg	Carbonate mg/kg	FMO mg/kg	Organic mg/kg	FeO mg/kg	Residual mg/kg	SUM mg/kg	Digest mg/kg	SUM%D %	HA mg/kg	FA mg/kg
0-5cm	70.5	37.5	63.5	40.8	18.8	14.5	245.5	267	91.9	5.4	0.55
0-5cm	75.3	35.8	59.5	36.5	17.0	12.5	236.5	286	82.7	8.2	0.65
0-5cm	73.3	37.3	60.8	41.5	23.0	14.5	250.3	282	88.7	5.25	0.6
0-5cm	74.3	37.0	69.5	49.5	28.2	16.5	275.0	243	113.2	8.05	0.55
0-5cm	73.0	36.8	62.7	46.3	20.8	16.8	256.3	238	107.7	4	0.65
0-5cm	76.0	39.3	64.3	47.8	21.5	16.3	265.0	254	104.3	4.25	0.65
5-10cm	93.5	38.8	77.3	47.5	27.8	16.0	300.8	291	103.4	10.95	0.8
5-10cm	90.5	37.0	74.5	44.3	29.5	17.5	293.3	283	103.6	10	0.55
5-10cm	92.0	38.3	76.3	43.3	28.2	15.8	293.8	291	100.9	7.6	0.75
5-10cm	90.5	38.8	71.0	41.5	27.3	13.0	282.0	293	96.2	11.15	0.9
5-10cm	91.3	37.8	76.8	44.3	26.3	15.3	291.5	282	103.4	10.3	0.85
5-10cm	93.0	35.3	75.8	45.5	29.0	17.5	296.0	292	101.4	10.75	0.75
10-15cm	82.8	31.8	65.5	45.5	191.3	271.8	688.5	630	109.3	11.8	0.45
10-15cm	76.3	32.0	64.0	42.5	165.5	220.8	601.0	618	97.2	8.75	0.35
10-15cm	74.8	29.5	60.0	36.0	91.8	135.0	427.0	633	67.5	7.35	0.5
10-15cm	78.0	33.0	67.0	46.3	153.3	209.8	587.3	663	88.6	12.95	0.4
10-15cm	78.5	56.3	70.8	44.3	144.3	165.3	559.3	654	85.5	13.95	0.35
10-15cm	80.5	33.5	71.0	54.5	186.0	265.3	690.8	651	106.1	10.35	0.45
15-25cm	79.3	35.3	78.0	42.8	81.8	99.0	416.0	468	88.9	6.3	0.3
15-25cm	82.8	35.8	82.8	47.3	68.8	87.0	404.3	480	84.2	4.85	0.4
15-25cm	83.3	35.3	78.0	42.0	86.3	110.3	435.0	472	92.2	4	1.1
15-25cm	77.5	38.3	78.3	45.0	100.0	142.3	481.3	472	102.0	3.75	0.65
15-25cm	81.5	37.8	84.8	50.5	116.0	161.8	532.3	468	113.7	5.45	0.5
15-25cm	81.0	35.8	74.3	45.8	101.3	141.8	479.8	470	102.1	4.75	1
25-35cm	81.3	36.0	78.5	43.0	33.5	45.3	317.5	362	87.7	4.45	0.4
25-35cm	78.8	37.0	76.3	46.5	24.8	28.0	291.3	380	76.6	4.85	0.45
25-35cm	81.0	35.0	71.8	41.8	57.5	88.0	375.0	378	99.2	15.7	0.5
25-35cm	79.8	35.0	71.3	43.0	35.3	45.8	310.0	343	90.4	21.5	0.5
25-35cm	82.5	33.5	71.8	42.0	24.8	25.0	279.5	348	80.3	13.45	0.4
25-35cm	79.5	33.5	70.3	41.8	34.3	43.5	302.8	357	84.8	0.6	0.5
35-50cm	60.8	37.5	77.8	38.8	35.0	50.0	299.8	309	97.0	4.85	0.45
35-50cm	60.0	36.0	79.5	38.3	42.0	62.5	318.3	324	98.2	4.05	0.5
35-50cm	62.5	34.8	79.3	41.3	31.5	45.5	294.8	312	94.5	4.1	0.5
35-50cm	63.7	35.8	71.0	40.0	28.5	42.0	281.0	326	86.2	4.55	0.45
35-50cm	64.0	36.0	82.3	40.8	64.0	100.3	387.3	321	120.6	4.85	0.5
35-50cm	65.3	35.3	77.8	41.3	51.5	72.5	343.5	315	109.0	4.95	0.5

	LOI %	HA g g	FA g g	pH	OC %	CEC me/100g	PYR10Fe mg/kg Fe	PYR7Fe mg/kg	PYR10 mg/kg	PYR7 mg/kg	NaOH mg/kg
0-5cm	17.9	0.03058	0.01794	4.1	10.4	23.35	4110	4810	219	224	60.5
0-5cm	18.8	0.01996	0.01598	4.3	10.2	25.2	4260	4890	226	233	63
0-5cm	19.3	0.02458	0.01078	4.2	10.1	24.4	4000	4660	218	228	61
0-5cm	18.2	0.03114	0.0183	4.2	10.2	24.65	3810	4580	208	225	65
0-5cm	18.5	0.02062	0.01746	4.1	10	23.9	4100	4600	216	223	62.5
0-5cm	18.8	0.02646	0.01238	4	10.7	24.25	4200	4600	220	226	61
5-10cm	11	0.02438	0.01992	3.9	7.9	13.4	4820	5320	213	235	58
5-10cm	11.1	0.02412	0.0096	4	7.5	10.65	4780	5100	210	230	61.5
5-10cm	10.7	0.02966	0.01124	3.9	7.2	11.75	4930	5600	219	253	63
5-10cm	10.6	0.02748	0.0089	3.9	7.5	11.3	4980	5170	214	234	60.5
5-10cm	10.5	0.02566	0.01546	3.9	7.8	15.45	4810	5320	216	243	59
5-10cm	10.2	0.0289	0.01264	3.9	7.2	13.75	4820	5130	210	229	60
10-15cm	8.5	0.04052	0.02354	3.8	5.1	12.8	5530	5720	198	215	54
10-15cm	8.7	0.0239	0.0084	3.8	5.4	13.9	5570	5600	199	212	52
10-15cm	8.9	0.03034	0.00956	3.9	5.1	16.3	5620	5610	202	215	50
10-15cm	9.3	0.04428	0.00916	4	5.1	13.9	5650	5860	206	223	54
10-15cm	9.2	0.0238	0.01708	3.8	5.3	20.95	5490	5670	207	217	61
10-15cm	9.2	0.02718	0.01158	3.8	5.1	16.7	5520	5550	199	217	55
15-25cm	7.8	0.0228	0.00544	3.8	4.8	12.2	5170	5200	200	218	48
15-25cm	7.9	0.01844	0.00602	3.8	5.1	14	5080	5410	194	226	50
15-25cm	7.8	0.01782	0.00842	3.8	5.1	12.8	5080	5330	196	227	52
15-25cm	7.6	0.01658	0.00788	3.8	5	12.85	4940	5330	192	222	42
15-25cm	7.6	0.02226	0.00724	3.8	4.8	13	4900	5170	194	221	48
15-25cm	7	0.02246	0.00762	3.8	5	13.15	5260	5270	209	226	46
25-35cm	7.2	0.02066	0.0058	3.9	5.8	14	4890	5220	211	243	48
25-35cm	7.7	0.02158	0.00726	3.8	5.2	12.2	4930	4940	211	227	48
25-35cm	8.2	0.06724	0.00564	3.9	5.3	13.2	4750	5200	207	236	48
25-35cm	8.3	0.10124	0.0082	4	5.3	14.4	4770	5360	208	246	48
25-35cm	8.3	0.02216	0.00598	3.9	5.2	14.4	4740	5150	208	234	54
25-35cm	8.3	0.0417	0.00672	3.8	5.4	13.65	5720	5320	244	247	50
35-50cm	7.1	0.01982	0.00408	4.2	3.6	12.1	5050	5970	179	227	36
35-50cm	7.1	0.01812	0.00528	4.3	3.6	12.75	4960	5600	177	217	38
35-50cm	6.9	0.01616	0.00488	4.2	3.4	12.25	5040	5140	180	206	36
35-50cm	7	0.01728	0.00608	4.2	3.4	14.6	4990	5070	184	201	36
35-50cm	6.5	0.01866	0.00418	4.2	3.5	12.9	4970	4930	181	195	36
35-50cm	6.1	0.01736	0.00372	4.1	3.5	12.25	5260	5160	185	214	38

RINGINGLOW Site SRG Zinc

Profile	Exchange mg/kg	Carbonate mg/kg	FMO mg/kg	Organic mg/kg	FeO mg/kg	Residual mg/kg	SUM mg/kg	Digest mg/kg	SUM%D %	HA mg/kg	FA mg/kg
0-5cm	12.8	4.3	7.2	5.3	4.5	19.0	53.0	63	84.1	1	0.25
0-5cm	13.0	4.3	7.0	5.3	5.8	18.3	53.5	65	82.3	0.9	0.55
0-5cm	13.0	4.5	7.2	5.3	7.5	18.5	56.0	64	87.5	1.25	0.2
0-5cm	13.0	4.3	7.5	6.3	10.5	19.0	60.5	66	91.7	1.1	0.1
0-5cm	13.0	4.3	7.2	6.0	3.5	21.5	55.5	64	86.7	0.95	0.45
0-5cm	12.5	4.5	7.2	6.5	4.0	22.0	56.8	66	86.0	1.1	0.3
5-10cm	7.2	2.5	5.5	4.8	9.0	21.8	50.8	56	90.6	1.7	0.25
5-10cm	7.0	2.3	5.5	4.8	11.0	21.5	52.0	56	92.9	1.5	0.25
5-10cm	7.0	2.3	5.8	4.8	11.0	20.5	51.3	56	91.5	0.8	0.3
5-10cm	6.8	2.5	5.5	5.0	11.5	19.3	50.5	55	91.8	1.4	0.3
5-10cm	7.0	2.3	5.5	5.3	7.2	22.3	49.5	55	90.0	0.95	0.3
5-10cm	7.2	2.3	5.5	4.8	9.3	22.5	51.5	57	90.4	0.85	0.25
10-15cm	6.3	2.3	4.8	3.8	3.0	21.5	41.5	52	79.8	1.7	0.25
10-15cm	6.0	2.3	4.8	3.8	3.0	19.8	39.5	52	76.0	1.35	0.25
10-15cm	6.0	2.3	5.0	4.0	3.0	23.5	43.8	52	84.1	1.25	0.25
10-15cm	6.0	2.3	5.0	4.0	3.3	22.8	43.3	57	75.9	1.65	0.25
10-15cm	6.3	2.3	5.0	4.5	3.3	20.3	41.5	52	79.8	1.45	0.25
10-15cm	6.3	2.3	5.3	4.0	2.8	22.8	43.3	50	86.5	1.4	0.3
15-25cm	6.5	3.3	7.5	5.0	3.8	29.8	55.8	57	97.8	0.95	0.25
15-25cm	7.0	3.0	7.5	5.3	3.5	31.8	58.0	62	93.5	0.8	0.25
15-25cm	6.8	3.0	7.5	5.3	3.5	29.5	55.5	57	97.4	0.9	0.4
15-25cm	6.8	3.0	7.2	5.3	3.5	31.8	57.5	56	102.7	0.9	0.3
15-25cm	6.8	2.8	7.2	5.3	3.8	31.8	57.5	57	100.9	0.85	0.35
15-25cm	6.8	2.8	7.0	5.0	3.5	32.0	57.0	55	103.6	1.05	0.3
25-35cm	12.5	4.3	10.0	7.2	4.0	33.3	71.3	70	101.8	1.1	0.25
25-35cm	11.0	4.0	10.0	6.5	3.8	30.8	66.0	75	88.0	1.25	0.25
25-35cm	11.3	4.0	9.8	6.3	3.8	33.3	68.3	69	98.9	4.15	0.3
25-35cm	11.3	4.0	10.0	6.5	3.8	34.0	69.5	67	103.7	2.9	0.25
25-35cm	11.0	4.3	9.5	6.0	3.8	28.2	62.8	68	92.3	1.75	0.25
25-35cm	11.0	3.8	9.8	6.5	4.0	35.5	70.5	69	102.2	1.5	0.25
35-50cm	14.2	5.8	13.0	6.5	4.3	31.8	75.5	76	99.3	1.6	0.3
35-50cm	14.2	5.8	13.3	6.8	4.0	33.8	77.8	78	99.7	1.5	0.25
35-50cm	14.8	5.3	13.5	6.8	3.8	35.5	79.5	76	104.6	1.1	0.3
35-50cm	14.5	5.5	11.8	6.3	3.8	34.3	76.0	77	98.7	1.35	0.3
35-50cm	14.8	5.5	13.3	6.5	4.0	33.0	77.0	77	100.0	1.9	0.3
35-50cm	14.8	5.5	13.3	7.2	3.8	34.0	78.5	78	100.6	0.85	0.3

	LOI %	HA g g	FA g g	pH	OC %	CEC me/100g	PYR10Fe mg/kg Fe	PYR7Fe mg/kg	PYR10 mg/kg	PYR7 mg/kg	NaOH mg/kg
0-5cm	17.9	0.03058	0.01794	4.1	10.4	23.35	4110	4810	84	86	10
0-5cm	18.8	0.01996	0.01598	4.3	10.2	25.2	4260	4890	83	87	9
0-5cm	19.3	0.02458	0.01078	4.2	10.1	24.4	4000	4660	83	86	9
0-5cm	18.2	0.03114	0.0183	4.2	10.2	24.65	3810	4580	82	85	9
0-5cm	18.5	0.02062	0.01746	4.1	10	23.9	4100	4600	82	86	9
0-5cm	18.8	0.02646	0.01238	4	10.7	24.25	4200	4600	82	86	10
5-10cm	11	0.02438	0.01992	3.9	7.9	13.4	4820	5320	68	74	7
5-10cm	11.1	0.02412	0.0096	4	7.5	10.65	4780	5100	68	74	7
5-10cm	10.7	0.02966	0.01124	3.9	7.2	11.75	4930	5600	69	75	7
5-10cm	10.6	0.02748	0.0089	3.9	7.5	11.3	4980	5170	69	74	7
5-10cm	10.5	0.02566	0.01546	3.9	7.8	15.45	4810	5320	68	76	6.5
5-10cm	10.2	0.0289	0.01264	3.9	7.2	13.75	4820	5130	69	73	7.5
10-15cm	8.5	0.04052	0.02354	3.8	5.1	12.8	5530	5720	66	71	6.5
10-15cm	8.7	0.0239	0.0084	3.8	5.4	13.9	5570	5600	67	70	6
10-15cm	8.9	0.03034	0.00956	3.9	5.1	16.3	5620	5610	66	70	6
10-15cm	9.3	0.04428	0.00916	4	5.1	13.9	5650	5860	67	71	5.5
10-15cm	9.2	0.0238	0.01708	3.8	5.3	20.95	5490	5670	71	71	6
10-15cm	9.2	0.02718	0.01158	3.8	5.1	16.7	5520	5550	66	70	5.5
15-25cm	7.8	0.0228	0.00544	3.8	4.8	12.2	5170	5200	64	70	6
15-25cm	7.9	0.01844	0.00602	3.8	5.1	14	5080	5410	64	70	6
15-25cm	7.8	0.01782	0.00842	3.8	5.1	12.8	5080	5330	64	72	6
15-25cm	7.6	0.01658	0.00788	3.8	5	12.85	4940	5330	64	70	6
15-25cm	7.6	0.02226	0.00724	3.8	4.8	13	4900	5170	64	70	6
15-25cm	7	0.02246	0.00762	3.8	5	13.15	5260	5270	66	70	6
25-35cm	7.2	0.02066	0.0058	3.9	5.8	14	4890	5220	75	83	8
25-35cm	7.7	0.02158	0.00726	3.8	5.2	12.2	4930	4940	75	81	7.5
25-35cm	8.2	0.06724	0.00564	3.9	5.3	13.2	4750	5200	74	79	7.5
25-35cm	8.3	0.10124	0.0082	4	5.3	14.4	4770	5360	75	82	7
25-35cm	8.3	0.02216	0.00598	3.9	5.2	14.4	4740	5150	74	80	8
25-35cm	8.3	0.0417	0.00672	3.8	5.4	13.65	5720	5320	78	84	7
35-50cm	7.1	0.01982	0.00408	4.2	3.6	12.1	5050	5970	80	88	7.5
35-50cm	7.1	0.01812	0.00528	4.3	3.6	12.75	4960	5600	79	87	7.5
35-50cm	6.9	0.01616	0.00488	4.2	3.4	12.25	5040	5140	80	85	7
35-50cm	7	0.01728	0.00608	4.2	3.4	14.6	4990	5070	82	86	7
35-50cm	6.5	0.01866	0.00418	4.2	3.5	12.9	4970	4930	80	84	7
35-50cm	6.1	0.01736	0.00372	4.1	3.5	12.25	5260	5160	82	85	7.5

RINGINGLOW Site SRG Copper

Profile	Exchange mg/kg	Carbonate mg/kg	FMO mg/kg	Organic mg/kg	FeO mg/kg	Residual mg/kg	SUM mg/kg	Digest mg/kg	SUM%D %	HA mg/kg	FA mg/kg
0-5cm	2.8	2.3	1.8	15.8	3.3	6.3	32.0	36	88.9	4.35	0.6
0-5cm	3.0	1.8	1.8	15.0	4.0	6.3	31.8	36	88.2	4.65	0.75
0-5cm	2.8	2.3	1.8	16.8	4.5	6.5	34.5	37	93.2	5.3	0.65
0-5cm	2.8	1.8	2.0	19.5	6.0	7.0	39.0	38	102.6	4.65	0.55
0-5cm	2.8	2.0	2.0	17.8	3.8	7.2	35.5	37	95.9	5.6	0.6
0-5cm	2.8	2.0	2.3	18.3	3.8	7.0	36.0	40	90.0	4.65	0.7
5-10cm	3.3	3.0	2.5	19.0	5.8	7.5	41.0	39	105.1	6.85	1
5-10cm	3.0	2.5	2.5	18.3	7.0	7.2	40.5	39	103.8	7.15	0.95
5-10cm	3.0	2.8	2.8	18.5	6.5	6.8	40.3	39	103.2	6.3	1.05
5-10cm	3.3	2.8	2.8	19.0	6.8	7.2	41.8	38	109.9	6.65	1.05
5-10cm	3.5	2.8	3.0	19.8	6.0	8.8	43.8	38	115.1	7.25	0.95
5-10cm	3.3	3.0	3.0	19.5	7.0	8.3	44.0	40	110.0	6.75	1.05
10-15cm	4.0	3.0	3.5	16.8	4.0	7.2	38.5	37	104.1	7	1
10-15cm	3.3	3.3	3.3	17.8	4.5	6.8	38.8	36	107.6	6.4	0.75
10-15cm	2.8	3.8	4.0	18.8	4.5	7.8	41.5	37	112.2	6.5	0.8
10-15cm	3.8	4.0	4.0	18.5	5.3	8.5	44.0	38	115.8	6.35	0.9
10-15cm	3.8	4.3	4.3	18.8	5.3	7.2	43.5	39	111.5	7	0.9
10-15cm	4.3	4.3	4.5	18.8	10.0	8.8	50.5	40	126.3	7.05	0.75
15-25cm	2.5	3.5	3.5	16.3	4.5	9.8	40.0	35	114.3	5.8	0.7
15-25cm	2.8	3.8	3.3	17.8	4.3	8.3	40.0	36	111.1	4.65	0.8
15-25cm	3.8	4.0	3.8	16.3	4.8	7.8	40.3	36	111.8	4.1	0.9
15-25cm	3.3	4.3	4.3	17.5	4.8	8.3	42.3	37	114.2	5.65	0.9
15-25cm	3.3	4.5	4.5	18.3	5.3	8.8	44.5	36	123.6	4.4	0.85
15-25cm	4.0	4.5	5.0	17.5	5.5	9.3	45.8	38	120.4	5.5	0.75
25-35cm	3.0	3.0	3.0	17.0	3.3	7.0	36.3	36	100.7	4.6	0.65
25-35cm	3.3	3.3	3.3	16.8	3.8	6.3	36.5	37	98.6	4.9	0.65
25-35cm	3.5	3.3	3.3	16.3	3.8	7.2	37.3	35	106.4	6.15	0.7
25-35cm	3.5	3.5	3.8	17.8	4.0	8.0	40.5	38	106.6	6.9	0.65
25-35cm	3.8	3.8	4.3	17.5	4.3	6.8	40.3	37	108.8	4.8	0.7
25-35cm	4.0	4.3	4.0	17.8	4.8	8.5	43.3	38	113.8	5.05	0.65
35-50cm	3.5	2.8	3.5	14.5	3.5	7.5	35.3	31	113.7	5	2
35-50cm	2.5	3.3	3.3	14.5	3.8	7.8	35.0	33	106.1	3.95	0.7
35-50cm	3.3	3.5	3.8	15.3	4.0	8.5	38.3	31	123.4	4.2	0.75
35-50cm	3.0	3.5	4.3	14.5	3.5	8.8	37.5	34	110.3	4.45	0.25
35-50cm	3.3	3.3	4.3	14.5	4.3	8.3	37.8	37	102.0	4.05	0.25
35-50cm	3.3	4.0	4.8	15.8	4.3	9.0	41.0	35	117.1	4.75	0.95

	LOI %	HA g g	FA g g	pH	OC %	CEC me/100g	PYR10Fe mg/kg Fe	PYR7Fe mg/kg	PYR10 mg/kg	PYR7 mg/kg	NaOH mg/kg
0-5cm	17.9	0.03058	0.01794	4.1	10.4	23.35	4110	4810	24	23	25
0-5cm	18.8	0.01996	0.01598	4.3	10.2	25.2	4260	4890	23	23	21.5
0-5cm	19.3	0.02458	0.01078	4.2	10.1	24.4	4000	4660	23	22	27.5
0-5cm	18.2	0.03114	0.0183	4.2	10.2	24.65	3810	4580	23	22	22
0-5cm	18.5	0.02062	0.01746	4.1	10	23.9	4100	4600	22	22	22
0-5cm	18.8	0.02646	0.01238	4	10.7	24.25	4200	4600	24	22	23
5-10cm	11	0.02438	0.01992	3.9	7.9	13.4	4820	5320	25	31	25
5-10cm	11.1	0.02412	0.0096	4	7.5	10.65	4780	5100	26	25	24.5
5-10cm	10.7	0.02966	0.01124	3.9	7.2	11.75	4930	5600	26	27	25
5-10cm	10.6	0.02748	0.0089	3.9	7.5	11.3	4980	5170	27	27	25
5-10cm	10.5	0.02566	0.01546	3.9	7.8	15.45	4810	5320	25	32	24.5
5-10cm	10.2	0.0289	0.01264	3.9	7.2	13.75	4820	5130	25	22	25
10-15cm	8.5	0.04052	0.02354	3.8	5.1	12.8	5530	5720	27	26	26
10-15cm	8.7	0.0239	0.0084	3.8	5.4	13.9	5570	5600	27	27	24.5
10-15cm	8.9	0.03034	0.00956	3.9	5.1	16.3	5620	5610	28	26	25.5
10-15cm	9.3	0.04428	0.00916	4	5.1	13.9	5650	5860	27	27	25
10-15cm	9.2	0.0238	0.01708	3.8	5.3	20.95	5490	5670	26	26	22.5
10-15cm	9.2	0.02718	0.01158	3.8	5.1	16.7	5520	5550	29	27	25.5
15-25cm	7.8	0.0228	0.00544	3.8	4.8	12.2	5170	5200	25	25	23
15-25cm	7.9	0.01844	0.00602	3.8	5.1	14	5080	5410	23	26	23
15-25cm	7.8	0.01782	0.00842	3.8	5.1	12.8	5080	5330	24	28	25
15-25cm	7.6	0.01658	0.00788	3.8	5	12.85	4940	5330	25	26	25.5
15-25cm	7.6	0.02226	0.00724	3.8	4.8	13	4900	5170	25	25	25
15-25cm	7	0.02246	0.00762	3.8	5	13.15	5260	5270	25	25	24
25-35cm	7.2	0.02066	0.0058	3.9	5.8	14	4890	5220	25	28	23
25-35cm	7.7	0.02158	0.00726	3.8	5.2	12.2	4930	4940	26	25	21.5
25-35cm	8.2	0.06724	0.00564	3.9	5.3	13.2	4750	5200	24	26	23.5
25-35cm	8.3	0.10124	0.0082	4	5.3	14.4	4770	5360	24	27	22
25-35cm	8.3	0.02216	0.00598	3.9	5.2	14.4	4740	5150	25	26	21.5
25-35cm	8.3	0.0417	0.00672	3.8	5.4	13.65	5720	5320	27	28	22.5
35-50cm	7.1	0.01982	0.00408	4.2	3.6	12.1	5050	5970	22	24	19.5
35-50cm	7.1	0.01812	0.00528	4.3	3.6	12.75	4960	5600	21	24	19
35-50cm	6.9	0.01616	0.00488	4.2	3.4	12.25	5040	5140	22	23	19
35-50cm	7	0.01728	0.00608	4.2	3.4	14.6	4990	5070	25	23	19.5
35-50cm	6.5	0.01866	0.00418	4.2	3.5	12.9	4970	4930	22	24	19
35-50cm	6.1	0.01736	0.00372	4.1	3.5	12.25	5260	5160	22	25	19.5

RINGINGLOW Site SRG Nickel

Profile	Exchange mg/kg	Carbonate mg/kg	FMO mg/kg	Organic mg/kg	FeO mg/kg	Residual mg/kg	SUM mg/kg	Digest mg/kg	SUM%D %	HA mg/kg	FA mg/kg
0-5cm	5.5	2.8	0.8	1.8	2.8	18.0	31.5	96	32.8	0	1
0-5cm	4.5	3.0	0.0	1.8	3.0	34.0	46.3	41	112.8	0	1.4
0-5cm	4.5	3.5	0.5	1.8	2.5	28.5	41.3	50	82.5	0	0.5
0-5cm	4.8	3.3	0.8	2.3	5.3	33.5	49.8	49	101.5	0	1.6
0-5cm	4.8	4.0	1.3	5.8	2.0	33.8	51.5	39	132.1	0	0.55
0-5cm	50.0	4.0	1.3	5.3	2.8	24.5	87.8	38	230.9	0	0.2
5-10cm	4.0	2.8	1.0	1.5	2.5	18.5	30.3	62	48.8	0	0.4
5-10cm	4.3	3.3	1.0	2.5	6.8	15.5	33.3	39	85.3	0	0.35
5-10cm	4.5	2.8	1.3	2.5	3.0	11.3	25.3	34	74.3	0	0.35
5-10cm	4.0	3.0	1.3	2.8	3.0	15.3	29.3	33	88.6	0	0.5
5-10cm	4.3	3.0	1.5	3.5	2.8	17.0	32.0	57	56.1	0	0.6
5-10cm	4.8	3.5	2.0	3.3	4.3	33.8	51.5	61	84.4	0	0.55
10-15cm	3.5	3.0	0.3	1.3	1.0	31.0	40.0	55	72.7	0	0.7
10-15cm	4.3	3.5	0.8	1.8	1.0	18.0	29.3	40	73.1	0	0.55
10-15cm	4.3	3.5	2.0	2.0	1.5	34.5	47.8	34	140.4	0	0.45
10-15cm	5.5	3.5	1.8	2.8	2.8	30.0	46.3	32	144.5	0	0.65
10-15cm	6.0	3.3	2.3	3.3	2.5	43.8	61.0	56	108.9	0	0.6
10-15cm	5.0	2.8	2.3	3.8	3.3	38.3	55.3	58	95.3	0	0.65
15-25cm	4.0	3.8	0.3	1.0	0.8	18.5	28.3	36	78.5	0	0.9
15-25cm	3.8	3.8	0.5	1.3	0.3	23.0	32.5	48	67.7	0	0.3
15-25cm	4.3	4.0	1.0	1.8	0.5	32.3	43.8	42	104.2	0	1.35
15-25cm	4.8	4.0	1.3	1.8	1.0	24.3	37.0	45	82.2	0	0.2
15-25cm	5.0	3.5	0.8	1.8	0.8	27.5	39.3	48	81.8	0	0.6
15-25cm	4.3	3.8	1.0	1.5	0.3	37.8	48.5	39	124.4	0	1.4
25-35cm	5.0	3.3	1.0	4.3	1.3	31.5	46.3	39	118.6	0	2.05
25-35cm	4.5	3.8	1.3	1.0	1.0	39.3	50.8	93	54.6	0	0.9
25-35cm	3.8	3.5	1.3	0.8	1.5	21.3	32.0	33	97.0	0	2.35
25-35cm	4.8	3.3	1.8	0.8	1.0	23.8	35.3	63	56.0	0	1.05
25-35cm	4.5	3.8	1.3	0.8	2.0	20.8	33.0	39	84.6	0	0.45
25-35cm	4.3	3.8	1.8	1.5	1.0	25.3	37.5	45	83.3	0	1.2
35-50cm	5.0	3.8	0.0	0.0	0.0	54.3	63.0	48	131.3	0	2.55
35-50cm	4.5	4.0	0.0	0.0	0.0	21.8	30.3	51	59.3	0	0
35-50cm	4.5	3.0	0.0	0.0	0.0	41.8	49.3	42	117.3	0	0.55
35-50cm	4.0	2.5	0.0	0.0	0.0	22.5	29.0	54	53.7	0	0.8
35-50cm	4.5	2.5	0.0	0.0	0.0	35.3	42.3	51	82.8	0	1.45
35-50cm	4.5	2.8	0.0	0.0	0.0	22.5	29.8	45	66.1	0	1.35

	LOI %	HA g g	FA g g	pH	OC %	CEC me/100g	PYR10Fe mg/kg Fe	PYR7Fe mg/kg
0-5cm	17.9	0.03058	0.01794	4.1	10.4	23.35	4110	4810
0-5cm	18.8	0.01996	0.01598	4.3	10.2	25.2	4260	4890
0-5cm	19.3	0.02458	0.01078	4.2	10.1	24.4	4000	4660
0-5cm	18.2	0.03114	0.0183	4.2	10.2	24.65	3810	4580
0-5cm	18.5	0.02062	0.01746	4.1	10	23.9	4100	4600
0-5cm	18.8	0.02646	0.01238	4	10.7	24.25	4200	4600
5-10cm	11	0.02438	0.01992	3.9	7.9	13.4	4820	5320
5-10cm	11.1	0.02412	0.0096	4	7.5	10.65	4780	5100
5-10cm	10.7	0.02966	0.01124	3.9	7.2	11.75	4930	5600
5-10cm	10.6	0.02748	0.0089	3.9	7.5	11.3	4980	5170
5-10cm	10.5	0.02566	0.01546	3.9	7.8	15.45	4810	5320
5-10cm	10.2	0.0289	0.01264	3.9	7.2	13.75	4820	5130
10-15cm	8.5	0.04052	0.02354	3.8	5.1	12.8	5530	5720
10-15cm	8.7	0.0239	0.0084	3.8	5.4	13.9	5570	5600
10-15cm	8.9	0.03034	0.00956	3.9	5.1	16.3	5620	5610
10-15cm	9.3	0.04428	0.00916	4	5.1	13.9	5650	5860
10-15cm	9.2	0.0238	0.01708	3.8	5.3	20.95	5490	5670
10-15cm	9.2	0.02718	0.01158	3.8	5.1	16.7	5520	5550
15-25cm	7.8	0.0228	0.00544	3.8	4.8	12.2	5170	5200
15-25cm	7.9	0.01844	0.00602	3.8	5.1	14	5080	5410
15-25cm	7.8	0.01782	0.00842	3.8	5.1	12.8	5080	5330
15-25cm	7.6	0.01658	0.00788	3.8	5	12.85	4940	5330
15-25cm	7.6	0.02226	0.00724	3.8	4.8	13	4900	5170
15-25cm	7	0.02246	0.00762	3.8	5	13.15	5260	5270
25-35cm	7.2	0.02066	0.0058	3.9	5.8	14	4890	5220
25-35cm	7.7	0.02158	0.00726	3.8	5.2	12.2	4930	4940
25-35cm	8.2	0.06724	0.00564	3.9	5.3	13.2	4750	5200
25-35cm	8.3	0.10124	0.0082	4	5.3	14.4	4770	5360
25-35cm	8.3	0.02216	0.00598	3.9	5.2	14.4	4740	5150
25-35cm	8.3	0.0417	0.00672	3.8	5.4	13.65	5720	5320
35-50cm	7.1	0.01982	0.00408	4.2	3.6	12.1	5050	5970
35-50cm	7.1	0.01812	0.00528	4.3	3.6	12.75	4960	5600
35-50cm	6.9	0.01616	0.00488	4.2	3.4	12.25	5040	5140
35-50cm	7	0.01728	0.00608	4.2	3.4	14.6	4990	5070
35-50cm	6.5	0.01866	0.00418	4.2	3.5	12.9	4970	4930
35-50cm	6.1	0.01736	0.00372	4.1	3.5	12.25	5260	5160

RINGINGLOW Site SRG Iron

Profile	Exchange mg/kg	Carbonate mg/kg	FMO mg/kg	Organic mg/kg	FeO mg/kg	Residual mg/kg	SUM mg/kg	Digest mg/kg	SUM%D %	HA mg/kg	FA mg/kg
0-5cm	182.5	100.0	2327.5	1530.0	1282.5	5385.0	10807.5	13170	82.1	103.5	6
0-5cm	227.5	105.0	2295.0	1315.0	1532.5	5105.0	10580.0	13870	76.3	96.5	12
0-5cm	200.0	127.5	2377.5	1485.0	1957.5	4995.0	11142.5	13370	83.3	141.5	6.5
0-5cm	215.0	120.0	2480.0	1795.0	2787.5	5170.0	12567.5	13790	91.1	100	13.5
0-5cm	212.5	120.0	2310.0	1637.5	947.5	5947.5	11175.0	13170	84.9	122	11
0-5cm	212.5	140.0	2335.0	1697.5	1155.0	5987.5	11527.5	13920	82.8	84	12.5
5-10cm	192.5	127.5	3080.0	1177.5	3175.0	6245.0	13997.5	15630	89.6	313	11.5
5-10cm	175.0	145.0	3032.5	1180.0	3510.0	6112.5	14155.0	15730	90.0	253	8.5
5-10cm	197.5	172.5	3165.0	1200.0	3842.5	5580.0	14157.5	15620	90.6	130.5	4.5
5-10cm	190.0	160.0	3052.5	1212.5	3905.0	5502.5	14022.5	15320	91.5	292	7.5
5-10cm	207.5	170.0	3112.5	1235.0	2635.0	6252.5	13612.5	15350	88.7	243	6.5
5-10cm	200.0	155.0	3072.5	1257.5	3187.5	6250.0	14122.5	15820	89.3	124.5	8.5
10-15cm	177.5	187.5	3510.0	845.0	1545.0	6962.5	13227.5	13620	97.1	490.5	7
10-15cm	157.5	190.0	3545.0	892.5	1597.5	6572.5	12955.0	13800	93.9	372	6.5
10-15cm	145.0	172.5	3660.0	930.0	1675.0	7337.5	13920.0	13660	101.9	340	4.5
10-15cm	145.0	197.5	3647.5	932.5	1705.0	7320.0	13947.5	13930	100.1	304.5	7.5
10-15cm	155.0	187.5	3805.0	960.0	1632.5	5997.5	12737.5	13840	92.0	423	4.5
10-15cm	185.0	195.0	3670.0	890.0	1525.0	7110.0	13575.0	13170	103.1	281.5	5
15-25cm	147.5	182.5	3697.5	802.5	1720.0	7080.0	13630.0	15070	90.4	312.5	6.5
15-25cm	155.0	195.0	3655.0	882.5	1735.0	7867.5	14490.0	16030	90.4	124	8.5
15-25cm	150.0	180.0	3690.0	770.0	1665.0	7202.5	13657.5	15470	88.3	194	20
15-25cm	160.0	190.0	3690.0	790.0	1540.0	8180.0	14550.0	15530	93.7	114	8.5
15-25cm	140.0	185.0	3722.5	817.5	1687.5	8107.5	14660.0	15320	95.7	93	1
15-25cm	145.0	180.0	3585.0	780.0	1712.5	7490.0	13892.5	15280	90.9	315	12.5
25-35cm	135.0	160.0	3962.5	865.0	1520.0	8035.0	14677.5	15630	93.9	229	4
25-35cm	140.0	145.0	3817.5	852.5	1582.5	7715.0	14252.5	17120	83.3	291	5
25-35cm	142.5	162.5	3742.5	805.0	1532.5	8347.5	14732.5	15820	93.1	531	5.5
25-35cm	122.5	160.0	3710.0	875.0	1562.5	8162.5	14592.5	15170	96.2	545	3.5
25-35cm	147.5	165.0	3672.5	830.0	1475.0	6600.0	12890.0	15280	84.4	364.5	4.5
25-35cm	150.0	155.0	3755.0	830.0	1552.5	8305.0	14747.5	15840	93.1	118	5.5
35-50cm	90.0	150.0	4560.0	920.0	1565.0	6332.5	13617.5	14400	94.6	359	4
35-50cm	105.0	152.5	4625.0	822.5	1607.5	7227.5	14540.0	14270	101.9	302	10
35-50cm	105.0	142.5	4670.0	922.5	1620.0	6850.0	14310.0	14610	97.9	193.5	7
35-50cm	92.5	150.0	4062.5	855.0	1597.5	7275.0	14032.5	14470	97.0	177	6
35-50cm	167.5	142.5	4865.0	900.0	1617.5	6912.5	14605.0	14160	103.1	276.5	8
35-50cm	240.0	150.0	4682.5	905.0	1655.0	7115.0	14747.5	14800	99.6	196.5	11

	LOI %	HA g g	FA g g	pH	OC %	CEC me/100g	PYR10Fe mg/kg Fe	PYR7Fe mg/kg	PYR10 mg/kg	PYR7 mg/kg	NaOH mg/kg
0-5cm	17.9	0.03058	0.01794	4.1	10.4	23.35	4110	4810	1630	1002.5	627.5
0-5cm	18.8	0.01996	0.01598	4.3	10.2	25.2	4260	4890	1445	758.5	686.5
0-5cm	19.3	0.02458	0.01078	4.2	10.1	24.4	4000	4660	1530	507.5	1022.5
0-5cm	18.2	0.03114	0.0183	4.2	10.2	24.65	3810	4580	1495	655	840
0-5cm	18.5	0.02062	0.01746	4.1	10	23.9	4100	4600	1520	826	694
0-5cm	18.8	0.02646	0.01238	4	10.7	24.25	4200	4600	1560	607.5	952.5
5-10cm	11	0.02438	0.01992	3.9	7.9	13.4	4820	5320	2000	579	1421
5-10cm	11.1	0.02412	0.0096	4	7.5	10.65	4780	5100	1935	707	1228
5-10cm	10.7	0.02966	0.01124	3.9	7.2	11.75	4930	5600	1820	-98	1918
5-10cm	10.6	0.02748	0.0089	3.9	7.5	11.3	4980	5170	1955	55.5	1899.5
5-10cm	10.5	0.02566	0.01546	3.9	7.8	15.45	4810	5320	1790	487.5	1302.5
5-10cm	10.2	0.0289	0.01264	3.9	7.2	13.75	4820	5130	1840	1.5	1838.5
10-15cm	8.5	0.04052	0.02354	3.8	5.1	12.8	5530	5720	2050	382.5	1667.5
10-15cm	8.7	0.0239	0.0084	3.8	5.4	13.9	5570	5600	1915	-136	2051
10-15cm	8.9	0.03034	0.00956	3.9	5.1	16.3	5620	5610	1965	350.5	1614.5
10-15cm	9.3	0.04428	0.00916	4	5.1	13.9	5650	5860	1955	294	1661
10-15cm	9.2	0.0238	0.01708	3.8	5.3	20.95	5490	5670	1715	346	1369
10-15cm	9.2	0.02718	0.01158	3.8	5.1	16.7	5520	5550	1875	297.5	1577.5
15-25cm	7.8	0.0228	0.00544	3.8	4.8	12.2	5170	5200	1800	176.5	1623.5
15-25cm	7.9	0.01844	0.00602	3.8	5.1	14	5080	5410	1770	244.5	1525.5
15-25cm	7.8	0.01782	0.00842	3.8	5.1	12.8	5080	5330	1850	191.5	1658.5
15-25cm	7.6	0.01658	0.00788	3.8	5	12.85	4940	5330	1880	585.5	1294.5
15-25cm	7.6	0.02226	0.00724	3.8	4.8	13	4900	5170	1920	544	1376
15-25cm	7	0.02246	0.00762	3.8	5	13.15	5260	5270	1835	454	1381
25-35cm	7.2	0.02066	0.0058	3.9	5.8	14	4890	5220	1630	398.5	1231.5
25-35cm	7.7	0.02158	0.00726	3.8	5.2	12.2	4930	4940	1680	43.5	1636.5
25-35cm	8.2	0.06724	0.00564	3.9	5.3	13.2	4750	5200	1650	188	1462
25-35cm	8.3	0.10124	0.0082	4	5.3	14.4	4770	5360	1620	523	1097
25-35cm	8.3	0.02216	0.00598	3.9	5.2	14.4	4740	5150	1790	181.5	1608.5
25-35cm	8.3	0.0417	0.00672	3.8	5.4	13.65	5720	5320	1710	285.5	1424.5
35-50cm	7.1	0.01982	0.00408	4.2	3.6	12.1	5050	5970	1355	162	1193
35-50cm	7.1	0.01812	0.00528	4.3	3.6	12.75	4960	5600	1235	177	1058
35-50cm	6.9	0.01616	0.00488	4.2	3.4	12.25	5040	5140	1335	384.5	950.5
35-50cm	7	0.01728	0.00608	4.2	3.4	14.6	4990	5070	1275	-16	1291
35-50cm	6.5	0.01866	0.00418	4.2	3.5	12.9	4970	4930	1265	44.5	1220.5
35-50cm	6.1	0.01736	0.00372	4.1	3.5	12.25	5260	5160	1305	366.5	938.5

RINGINGLOW Site SRG Manganese

Profile	Exchange mg/kg	Carbonate mg/kg	FMO mg/kg	Organic mg/kg	FeO mg/kg	Residual mg/kg	SUM mg/kg	Digest mg/kg	SUM%D %	HA mg/kg	FA mg/kg
0-5cm	41.0	11.8	30.5	5.5	18.8	26.3	133.8	157	85.2	0	0.05
0-5cm	42.5	10.8	30.0	5.0	22.3	21.3	131.8	155	85.0	0	0.1
0-5cm	41.8	11.3	30.0	5.8	26.5	19.8	135.0	158	85.4	0	0.1
0-5cm	42.5	11.0	31.3	6.8	32.5	19.0	143.0	157	91.1	0	0.1
0-5cm	42.3	11.0	30.0	6.5	13.0	31.8	134.5	154	87.3	0	0.1
0-5cm	42.8	11.5	30.5	6.8	16.0	30.5	138.0	160	86.3	0	0.1
5-10cm	26.3	7.8	35.3	1.8	31.0	22.3	124.3	132	94.1	0	0.15
5-10cm	25.3	7.8	35.3	2.0	32.8	19.3	122.3	130	94.0	0	0.1
5-10cm	25.3	7.8	36.8	1.8	32.5	17.8	121.8	137	88.9	0	0.15
5-10cm	25.5	8.0	34.8	1.8	33.8	17.5	121.3	131	92.6	0	0.15
5-10cm	26.5	7.8	36.0	1.8	27.3	23.0	122.3	130	94.0	0	0.15
5-10cm	26.0	7.0	34.0	1.8	30.3	20.5	119.5	136	87.9	0	0.15
10-15cm	20.8	6.8	44.3	3.0	14.2	28.2	117.3	125	93.8	0	0.05
10-15cm	20.0	6.5	41.5	3.3	15.0	28.7	115.0	122	94.3	0	0.1
10-15cm	20.3	5.8	42.5	3.5	15.5	38.0	125.5	122	102.9	0	0.1
10-15cm	20.5	7.0	44.8	3.5	16.3	28.7	120.8	124	97.4	0	0.85
10-15cm	21.3	7.5	46.3	3.5	15.5	23.5	117.5	130	90.4	0	0.8
10-15cm	20.5	6.3	42.0	3.5	14.0	28.5	114.8	122	94.1	0	0.85
15-25cm	36.0	14.8	50.5	3.8	15.8	32.3	153.0	152	100.7	0	0.05
15-25cm	36.8	14.0	50.0	4.0	16.3	33.0	154.0	156	98.7	0	0.7
15-25cm	35.5	14.0	48.5	3.8	15.0	27.5	144.3	153	94.3	0	0.85
15-25cm	36.0	15.3	49.3	3.8	14.8	34.0	153.0	151	101.3	0	0.65
15-25cm	34.8	14.0	48.5	3.8	15.3	31.3	147.5	149	99.0	0	0.15
15-25cm	34.8	13.8	47.8	3.8	15.8	30.3	146.0	152	96.1	0	1.4
25-35cm	41.8	14.2	50.5	4.3	14.8	28.5	154.0	155	99.4	0	0.05
25-35cm	41.0	14.0	50.7	4.8	16.8	26.8	154.0	168	91.7	0	0.05
25-35cm	41.0	13.5	51.0	4.0	14.5	28.5	152.5	150	101.7	0	0.1
25-35cm	41.8	13.5	49.8	4.3	15.3	28.5	153.0	152	100.7	0	0.05
25-35cm	41.0	13.5	48.5	4.0	14.5	23.3	144.8	159	91.0	0	0.1
25-35cm	40.8	13.3	49.3	4.3	14.8	28.2	150.5	164	91.8	0	0.05
35-50cm	33.5	14.8	62.7	3.8	13.0	25.5	153.3	159	96.4	0	0.05
35-50cm	34.3	14.2	64.3	4.0	13.5	29.0	159.3	166	95.9	0	0.1
35-50cm	34.5	14.2	71.3	4.3	13.8	28.2	166.3	162	102.6	0	0.1
35-50cm	35.0	14.5	60.3	4.0	14.0	29.3	157.0	162	96.9	0	0.1
35-50cm	35.5	15.3	67.3	4.3	13.8	28.7	164.8	162	101.7	0	0.1
35-50cm	35.5	15.0	73.8	4.5	14.8	29.8	173.3	158	109.7	0	0.1

	LOI %	HA g g	FA g g	pH	OC %	CEC me/100g	PYR10Fe mg/kg Fe	PYR7Fe mg/kg
0-5cm	17.9	0.03058	0.01794	4.1	10.4	23.35	4110	4810
0-5cm	18.8	0.01996	0.01598	4.3	10.2	25.2	4260	4890
0-5cm	19.3	0.02458	0.01078	4.2	10.1	24.4	4000	4660
0-5cm	18.2	0.03114	0.0183	4.2	10.2	24.65	3810	4580
0-5cm	18.5	0.02062	0.01746	4.1	10	23.9	4100	4600
0-5cm	18.8	0.02646	0.01238	4	10.7	24.25	4200	4600
5-10cm	11	0.02438	0.01992	3.9	7.9	13.4	4820	5320
5-10cm	11.1	0.02412	0.0096	4	7.5	10.65	4780	5100
5-10cm	10.7	0.02966	0.01124	3.9	7.2	11.75	4930	5600
5-10cm	10.6	0.02748	0.0089	3.9	7.5	11.3	4980	5170
5-10cm	10.5	0.02566	0.01546	3.9	7.8	15.45	4810	5320
5-10cm	10.2	0.0289	0.01264	3.9	7.2	13.75	4820	5130
10-15cm	8.5	0.04052	0.02354	3.8	5.1	12.8	5530	5720
10-15cm	8.7	0.0239	0.0084	3.8	5.4	13.9	5570	5600
10-15cm	8.9	0.03034	0.00956	3.9	5.1	16.3	5620	5610
10-15cm	9.3	0.04428	0.00916	4	5.1	13.9	5650	5860
10-15cm	9.2	0.0238	0.01708	3.8	5.3	20.95	5490	5670
10-15cm	9.2	0.02718	0.01158	3.8	5.1	16.7	5520	5550
15-25cm	7.8	0.0228	0.00544	3.8	4.8	12.2	5170	5200
15-25cm	7.9	0.01844	0.00602	3.8	5.1	14	5080	5410
15-25cm	7.8	0.01782	0.00842	3.8	5.1	12.8	5080	5330
15-25cm	7.6	0.01658	0.00788	3.8	5	12.85	4940	5330
15-25cm	7.6	0.02226	0.00724	3.8	4.8	13	4900	5170
15-25cm	7	0.02246	0.00762	3.8	5	13.15	5260	5270
25-35cm	7.2	0.02066	0.0058	3.9	5.8	14	4890	5220
25-35cm	7.7	0.02158	0.00726	3.8	5.2	12.2	4930	4940
25-35cm	8.2	0.06724	0.00564	3.9	5.3	13.2	4750	5200
25-35cm	8.3	0.10124	0.0082	4	5.3	14.4	4770	5360
25-35cm	8.3	0.02216	0.00598	3.9	5.2	14.4	4740	5150
25-35cm	8.3	0.0417	0.00672	3.8	5.4	13.65	5720	5320
35-50cm	7.1	0.01982	0.00408	4.2	3.6	12.1	5050	5970
35-50cm	7.1	0.01812	0.00528	4.3	3.6	12.75	4960	5600
35-50cm	6.9	0.01616	0.00488	4.2	3.4	12.25	5040	5140
35-50cm	7	0.01728	0.00608	4.2	3.4	14.6	4990	5070
35-50cm	6.5	0.01866	0.00418	4.2	3.5	12.9	4970	4930
35-50cm	6.1	0.01736	0.00372	4.1	3.5	12.25	5260	5160